Journal
of the
Optical Society of America
and
Review of Scientific Instruments

Vol. 10 JUNE, 1925 Number 6

THE OPTICAL CONSTANTS OF CRYSTALS OF SELENIUM AND TELLURIUM FOR WAVE-LENGTHS FROM 3000 TO 5000 ANGSTROMS

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ABSTRACT

The measurements were made by a photographic method, for two positions of the crystal, (1) with the optic axis parallel, and (2) with the axis perpendicular to the plane of incidence. Two sets of optical constants were found for each substance. For selenium, in the parallel position the index of refraction was found to vary from 3.4 to 4.4, and the reflecting power from 0.38 to 0.46; in the perpendicular position the index varies from 2.3 to 3.1, and the reflecting power from 0.41 to 0.34. For tellurium, in the parallel position the index varies from 1.9 to 2.9, and the reflecting power from 0.10 to 0.27; in the perpendicular position the index varies from 1.7 to 2.7, the reflecting power from 0.09 to 0.23. The average error is estimated to be about 5 per cent. The accuracy is greatest for the middle range of wave-lengths, 3500-4000 A.

I. INTRODUCTION

When plane-polarized light is reflected from the polished surface of an absorbing medium it becomes in general elliptically polarized. The shape of the vibration ellipse formed by reflection depends upon the angle of incidence and upon the optical constants (coefficient of absorption and index of refraction) of the reflecting material. Equations have been developed by Drude[1] which connect the optical constants and angle of incidence with the phase angle and azimuth of the ellipse. Thus if the form of the elliptical vibration can be found for some known angle of incidence, the optical constants may be calculated.

There are two general methods of determining the vibration form of reflected light. The first is the polarimetric method, in which the constants of the ellipse are found visually with the aid of a Babinet compensator and analyzing Nicol. The second is an indirect photo-

[1] P. Drude: Ann. der Phys. *34*, p. 528; 1888.

graphic method, first suggested by Voigt.[2] This latter plan was followed in the present investigation.

It has been found experimentally by Tate[3] that the optical constants obtained by reflection vary considerably with the degree of polish of the metallic surface and the character of the polishing process. This difficulty may be avoided in case of certain substances by using the faces of crystals. There is another and more important advantage in the use of crystals. If the substance should be doubly refracting, it may be possible to determine two sets of optical constants by taking measurements with the axis of the crystal first in one direction and then in another direction at right angles to the first.

Selenium and tellurium are well adapted to use in this way, as they crystallize in slender hexagonal needles with faces which are often nearly perfect. Selenium has been investigated by Skinner[4] and Weld[5] for the visible spectrum, and found to be doubly refracting. Van Dyke[6] found the same to be true of tellurium.

The object of the present research was to find the optical constants of these two substances for the ultra violet region of the spectrum, and to check the work of Weld and Van Dyke for a part of the visible spectrum.

II. APPARATUS

The apparatus used was the Crystelliptometer described by Weld (loc. cit.[5]). The Hilger constant deviation monochromator used by Weld was replaced by one built according to plans given by Pfund,[7] and an iron arc of the Pfund[8] type was used as a source of light. The monochromator was not calibrated, but the wave-lengths were determined by identifying lines in the iron spectrum. In the ultra violet this was done by means of the fluorescence produced upon a thin plate of uranium glass.

The Crystelliptometer was accurately aligned with the beam of light from the polarizer by utilizing the telescope of the spectrometer upon which the crystal was mounted. A narrow beam, after passing through the telescope was observed through the camera tube of the Crystelliptometer, and the latter adjusted so that the beam was

[2] Voigt: Physik. Zeitschr. *2*, 203, 1901.
[3] J. T. Tate: Phys. Rev. *34*, p. 321; 1912.
[4] C. H. Skinner: Phys. Rev. N.S. *9*, p. 148; 1917.
[5] L. D. Weld: J. O. S. A. & R. S. I. *6*, p. 67; 1922.
[6] G. D. Van Dyke: J. O. S. A. & R. S. I. *6*, p. 919; 1922.
[7] A. Pfund: Phys. Rev. *7*, p. 291; 1916.
[8] A. Pfund: Astrophysical Jour. *27*, p. 296; 1908.

centered. The accurate alignment secured by this means prevented any shift of the spot-pattern with changes of focus and wave-length. When a photograph was desired with ultra violet light, all adjustments of the apparatus were made by aid of visible light, and then the wave-length was changed. A new crystal-mounting was constructed, which permitted adjustments about three mutually perpendicular axes. Two positions of the crystal were used: (1) axis horizontal (parallel to the plane of incidence); (2) axis vertical (perpendicular to the plane of incidence). The crystal could be turned from one of these positions to the other in its own plane, so that a photograph of the reflected beam could be secured with the crystal in each position successively with only one setting of the Crystelliptometer.

III. THEORY AND CALCULATIONS

Voigt (loc. cit.[2]) and Minor[9] give the following equations for the coordinates of any dark spot on a spot-pattern produced by a double wedge-system such as was used in this investigation: (see Figs. 1 and 2.)

$$\delta_1 = \delta' + \Delta = 2\pi n, \text{ or } \delta' = 2\pi n - \Delta \quad (1)$$

$$\theta_1 = -\psi + \beta \pm \tfrac{1}{2}(2n+1)\pi \quad (2)$$

$$\delta_2 = \delta'' + \Delta = (2n+1)\pi, \text{ or } \delta'' = (2n+1)\pi - \Delta \quad (3)$$

$$\theta_2 = +\psi + \beta \pm \tfrac{1}{2}(2n+1)\pi \quad (4)$$

In these equations Δ = difference of phase of the two components of the incident vibration, δ' and δ'' are the relative retardations introduced by the Babinet compensator, δ is the total phase difference, θ = angle of rotation in the second wedge-system (rotator) at the point of passage, β = angle between the x-axis and the plane of transmission of the analyzer, and ψ = azimuth of the plane-polarized light into which the elliptical vibration is changed by the wedge-system. n is any one of the sequence of numbers 0, 1, 2, 3, 4 . . . . . δ and θ may be used as the coordinates of a system of lines, with the δ-axis horizontal, and the θ-axis vertical. Equation (1) gives a system of lines parallel to the θ-axis, which are the loci of points where the light is plane-polarized. Equation (2) gives a set of lines parallel to the δ-axis, which are the loci of points where the aximuth of the plane-polarized vibration is perpendicular to the transmission-axis of the analyzer. The intersections of the lines (δ_1, θ_1) give points of zero intensity or dark spots. A second system of lines is given by equations (3) and (4), whose intersections (δ_2, θ_2) give points of zero intensity. These equations show

[9] Minor. Ann. der Phys. *10*, p. 581; 1903.

how the two systems of spots shift as changes are made in the phase angle Δ or the azimuth ψ of the incident light. If the relative phase Δ is changed by an amount Δ_1 then from equations (1) and (3),

$$\delta' = -\Delta + 2n\pi - \Delta_1, \text{ and } \delta'' = -\Delta + (2n+1)\pi - \Delta_1.$$

This shows that the δ-coordinate of each spot is changed by the same amount, so that the entire spot-pattern is shifted horizontally. The situation is quite different when ψ is changed. Let the amount of the change be ϵ. Then from equations (2) and (4),

$$\theta_1 = -(\psi+\epsilon)+\beta \pm \tfrac{1}{2}(2n+1)\pi = -\psi+\beta \pm \tfrac{1}{2}(2n+1)\pi - \epsilon.$$
$$\theta_2 = +(\psi+\epsilon)+\beta \pm \tfrac{1}{2}(2n+1)\pi = +\psi+\beta \pm \tfrac{1}{2}(2n+1)\pi + \epsilon.$$

This shows that the spots of the two systems are shifted vertically by the same amount but in opposite directions.

Application of the Equations to Data from Plate Measurements. Take as coordinate axes the lines where $\delta' = 0$, and $\theta = 0$. From eq. (1), when $n = 0$, $\delta_1 = 0$ and $\delta' = -\Delta$. Then if $\delta' = 0$, (along the y-axis) $\Delta = 0$. This means that the column of spots for which $\Delta = 0$ lies upon the y-axis.

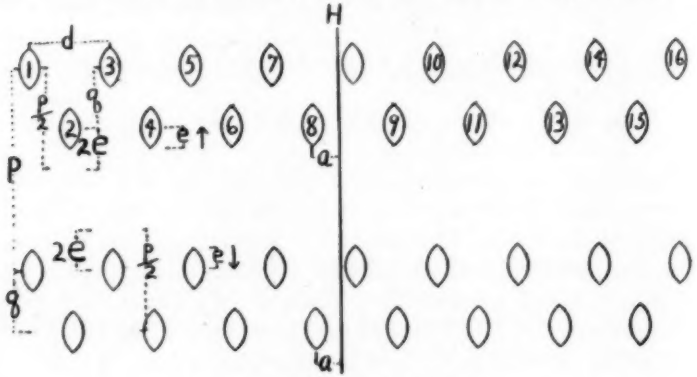

FIG. 1. *Sketch of a typical spot-pattern.*

This is the case for the comparison spot-pattern, photographed when a plane-polarized beam is admitted into the Crystelliptometer without reflection. But when the incident plane-polarized beam is reflected from a polished surface, (assuming no elliptical polarization) the plane of vibration, as seen by the observer, is rotated through 90 degrees. This is equivalent to a phase change $\Delta = \pi$ between the components of the original vibration. Then from eq. (1) $\delta' = -\pi$, which means that there has been a sidewise shift of the entire spot-pattern through a distance $d/2$, if d is defined as the distance between adjacent columns belonging to the same system. As may be seen from eq. (1), d corre-

sponds to a phase change of 2π. From eq. (3), when $n=0$ and $\Delta=\pi$, $\delta_2=0$. Thus we see that a column of spots belonging to the second system lies along the y-axis. For convenience in measurement this latter column was chosen as the "zero column," and all shifts referred to its position when $\Delta=\pi$. If the reflected beam is elliptically polarized, the relative phase difference between the components of the incident beam is Δ, and the change of phase compared to a plane-polarized reflected beam is $\pi-\Delta$. This change of phase results in a shift of the spot-pattern through a distance a. (See Fig. 1).

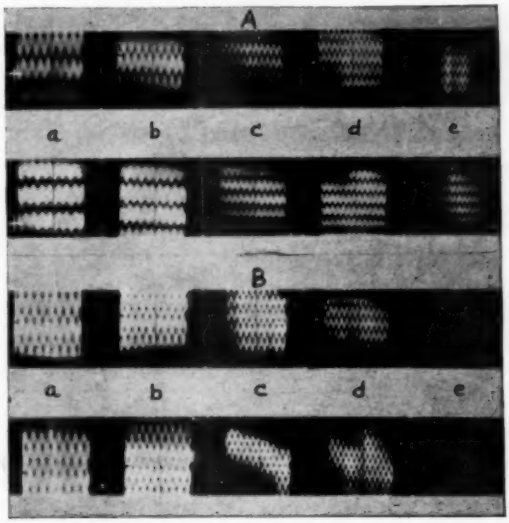

FIG. 2. *Photographs of spot-patterns of selenium (A), and tellurium (B).*
Upper row in each case, crystal axis parallel to the plane of incidence.
Lower row, crystal axis perpendicular to the plane of incidence. Wave-lengths in Angstroms: (a) 4529; (b) 4068; (c) 3440; (d) 3200; (e) 3008. Angle of incidence 70 degrees.

The phase-change may also be represented by the expression: $2\pi a/d$, since a shift d represents a change of phase of 2π. Thus $\pi-\Delta=a/d \times 360°$. As an example, plate 42H ($\lambda=3750$, $\phi=65°$), gives $a=0.196$; $d=1.624$ mm. Then $\pi-\Delta=\dfrac{0.196}{1.624}\times 360°=43.5°$, and $\Delta=136.5°$.

In eq. (2) let $\beta=0$, (transmission axis of the analyzer horizontal) and $\psi=\psi_0-\psi_1$. Then $\theta_1=-(\psi_0-\psi_1)\pm\frac{1}{2}(2n+1)\pi$. Here ψ_0 is the azimuth of the plane-polarized light incident upon a surface, and ψ_1

is the change in aximuth produced by the quartz wedges of the Crystel-liptometer. In practice ψ_0 was taken equal to 45°, so that $\theta_1=\psi_1-45°\pm\frac{1}{2}(2n+1)\pi$. Similarly from eq. (4), $\theta_2=\psi_1+45°\pm\frac{1}{2}(2n+1)\pi$. Thus the change in aximuth ψ_1 is proportional to the change in the y-coordinate θ. Represent this shift by e. Then a shift e means an azimuth change of $e/p\times180°$, since one vertical spot-interval p involves a change of 180° or π (see eq. 2). Thus $\psi_1=e/p\times180°$. Now

$$\psi=\psi_0-\psi_1=45°-\left(\frac{e}{p}\times180°\right) \tag{5}$$

It is very convenient to measure the distance q between adjacent rows rather than the y-coordinate of any spot. As shown in fig. 1, $q=p/2-2e$, or $e=(p-2q)$. Substituting in equation (5).

$$\psi=45°-\frac{p-2q}{4p}\times180°=\frac{q}{p}\times90°\,. \tag{6}$$

This is the relation used for calculating ψ. For example, plate 42H gives $q=1.08$; $p=4.32$ mm. Then $\psi=\dfrac{1.08}{4.32}\times90°=22.5°$.

Equations of the Optical Constants. Drude (loc. cit.[1]) has derived equations for the optical constants of doubly refracting crystalline substances, and their applicability in this connection has been discussed by Sieg.[10]

$$\frac{\cos 2\psi_1+i\sin 2\psi_1\sin\Delta_1}{1-\sin 2\psi_1\cos\Delta_1}=\frac{\sqrt{\alpha}}{\cos\phi}-\sqrt{\gamma}\cos\phi \tag{7}$$

$$\frac{\cos 2\psi_2+i\sin 2\psi_2\sin\Delta_2}{1-\sin 2\psi_2\cos\Delta_2}=\frac{\sqrt{\gamma}}{\cos\phi}-\sqrt{\alpha}\cos\phi \tag{8}$$

In these equations ϕ is the angle of incidence, ψ is the azimuth angle, Δ is the relative phase of the x and y components of the elliptical vibration, and α and γ are complex constants. The subscripts (1) and (2) refer to the two positions of the crystal, with axis respectively horizontal (parallel to the plane of incidence) and vertical (perpendicular to the plane of incidence).

Let

$$\alpha=A_{11}+iA_{12}\,;\quad \gamma=A_{31}+iA_{32}$$

[10] L. P. Sieg. J. O. S. A. & R. S. I. 6, p. 448; 1922.

Then if χ is such an angle that $\tan \chi = \frac{A_{12}}{A_{11}}$, and if $\tan \Sigma = \frac{A_{32}}{A_{31}}$, then

$$K_1 = \tan \frac{\chi}{2}, \text{ and } K_2 = \tan \frac{\Sigma}{2} \tag{9}$$

Here K_1 and K_2 are the absorption coefficients.

$$N_1^2 = \frac{2 \sin \frac{\chi}{2} \cos^3 \frac{\chi}{2}}{A_{12}}; \quad N_2^2 = \frac{2 \sin \frac{\Sigma}{2} \cos^3 \frac{\Sigma}{2}}{A_{32}} \tag{10}$$

N_1 and N_2 are the indices of refraction.

$$R_1 = \frac{N_1^2(1+K_1^2)+1-2N_1}{N_1^2(1+K_1^2)+1+2N_1}; \quad R_2 = \frac{N_2^2(1+K_2^2)+1-2N_2}{N_2^2(1+K_2^2)+1+2N_2} \tag{11}$$

R_1 and R_2 are the coefficients of reflection, or reflecting powers.

A Sample Calculation of the Optical Constants. Assume the following data, obtained from plates 77H and 77V, by the method previously described: (The crystal was selenium). $\phi = 75°$; $\Delta_1 = 106.7°$; $\psi_1 = 14.8°$; $\cos 2\psi_1 = 0.8695$; $\sin 2\psi_1 = 0.494$; $\cos \Delta_1 = -0.2874$; $\sin \Delta_1 = 0.958$; $\Delta_2 = 69°$; $\psi_2 = 13.8°$; $\cos 2\psi_2 = 0.8862$; $\sin 2\psi_2 = 0.4633$; $\cos \Delta_2 = 0.3584$; $\sin \Delta_2 = 0.9336$; $\cos \phi = 0.2588$. Substituting in eqs. (7) and (8),

$$\frac{0.8695 + i\,0.494 \times 0.958}{1-(0.494 \times -0.2874)} = \frac{\sqrt{\alpha}}{0.2588} - 0.2588\sqrt{\gamma}$$

$$\frac{0.8862 + i\,0.4633 \times 0.9336}{1-(0.4633 \times 0.3584)} = \frac{\sqrt{\gamma}}{0.2588} - 0.2588\sqrt{\alpha}$$

From which $\alpha = 0.0225 + i\,0.0342$, and $\gamma = 0.062 + i\,0.0806$. Substituting values of A_{11}, A_{12}, A_{31}, A_{32}, in eq. (9), $K_1 = 0.539$, and $K_2 = 0.495$. From eq. (10),

$$N_1^2 = \frac{2 \times 0.475 \times 0.682}{0.0342} = 18.9; \quad N_1 = 4.35.$$

$$N_2^2 = \frac{2 \times 0.443 \times 0.72}{0.0806} = 7.9; \quad N_2 = 2.81.$$

Substituting values of N and K in eq. (11),

$$R_1 = \frac{(18.9 \times 1.29)+1-8.7}{(18.9 \times 1.29)+1+8.7} = 0.49; \quad R_2 = \frac{(7.9 \times 1.245)+1-5.6}{(7.9 \times 1.245)+1+5.6} = 0.32$$

Sample Data from Plate Measurements

Plate No. 42V, $\lambda = 3750$ A, $\phi = 65°$. (See FIG. 1).

x-coordinates of dark spots.				$x-x_0$ (−)	$x-x_0$ (+)	y-coordinates of rows.		
Hair	23.51		mm	mm	mm	mm	q	
1	17.21	9	24.50	6.30	0.99	24.77		
2	18.04	10	25.25	5.47	1.74	23.72	1.05	
3	18.79	11	26.10	4.71	2.59	20.53		
4	19.63	12	26.92	3.88	3.41	19.43	1.10	
5	20.48	13	27.75	3.03	4.24		1.08	Av.
6	21.29	14	28.51	2.22	5.00			
7	22.04	15	29.35	1.47	5.84			
8	22.84	16	30.18	0.67	6.67			
				27.75	30.48			
					−27.75			
				sum	2.73			

$d = 1.624$, from comparison plate.

$p = 4.32$, from comparison plate.

$a' = 2.73/16 = 0.17$ $\quad \pi - \Delta_2 = a/d \times 360° = 43.5°$ $\quad \Delta_2 = 136.5°$

c 0.026

a 0.196 $\quad \psi_2 = q/p \times 90° = 22.5°$

Explanation: a' is the sidewise shift, and is the algebraic sum of the x-coordinates divided by the number of spots measured. c is a correction which must be applied because the central column of spots may not lie exactly on the hair-line when $\phi = 0$. c is found in the same way as a', except that the plate is taken in the comparison position, i.e. the beam of plane-polarized light enters the Crystelliptometer directly without reflection. d and p are the average spot-intervals in the horizontal and vertical directions respectively. They may be obtained either from the data given above or from the comparison plate.

IV. TABLES OF OPTICAL CONSTANTS

TABLE 1. *Optical Constants of Selenium (averages). λ is the wave-length in Angstroms, K is the absorption coefficient, N is the index of refraction and R is the reflecting power. The subscripts (1) and (2) refer to the parallel and the perpendicular position respectively.*

λ	K_1	K_2	N_1	N_2	R_1	R_2
3008	0.47	0.93	3.4	2.3	0.38	0.41
3200	0.60	0.89	3.4	2.3	0.44	0.38
3440	0.80	0.79	3.6	2.6	0.51	0.36
3750	0.61	0.68	3.8	2.9	0.52	0.38
4068	0.86	0.46	3.6	3.3	0.54	0.36
4529	0.51	0.41	4.4	3.1	0.46	0.34
4958	0.60	0.57	3.4	3.4	0.42	0.26

Each value given in the tables is the average of four separate determinations, each made for a different angle of incidence, ranging from 55° to 80°. Two plates are required for each angle of incidence, and

one or two additional plates are taken in the comparison position. Thus each determination of the optical constants involved the exposure and measurement of nine or ten photographic plates. Each column of

TABLE 2. *Optical Constants of Tellurium (averages). Symbols have the same meaning as in Table I.*

λ	K_1	K_2	N_1	N_2	R_1	R_2
3008	0.09	0.30	1.9	1.66	0.10	0.09
3200	0.14	0.32	2.1	1.6	0.14	0.12
3440	0.13	0.35	2.4	1.9	0.18	0.15
3750	0.17	0.35	2.5	2.0	0.21	0.16
4068	0.21	0.37	2.8	2.4	0.24	0.22
4529	0.26	0.42	3.1	2.8	0.30	0.29
4900	0.24	0.34	2.9	2.7	0.27	0.23

spots was measured at least three times, and each row (y-coordinates) five times. The values of the coordinates given in the sample data are averages.

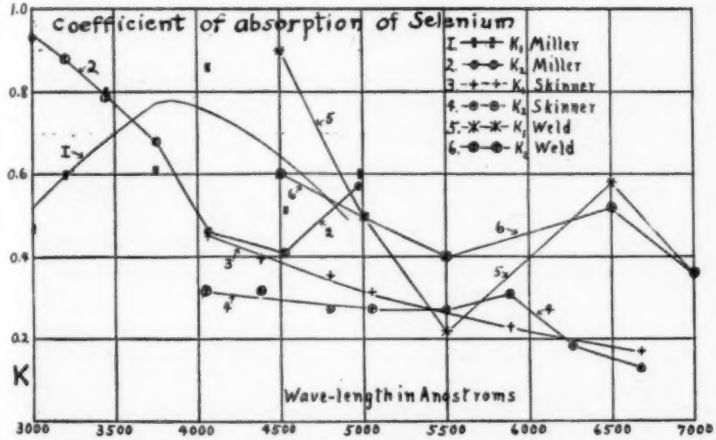

FIG. 3. *Coefficients of absorption of selenium, as found by three investigators. The subscripts (1) and (2) refer to the parallel and the perpendicular position of the crystal respectively.*

V. DISCUSSION OF ERRORS

The chief errors involved are (1) imperfect adjustment of the apparatus, and (2) errors of judgment in estimating the positions of the centers of the dark spots when measuring their coordinates with the comparator microscope. Errors of the latter kind may be estimated by noting the deviation from the average. The quantities d and p

can be measured more accurately than a or q, and usually their values obtained from several plates at the same wave-length agree to one part in 150 or 200. q is hard to measure because the spots are elongated and sometimes triangular, so that the centers are hard to locate. a is a small quantity, often only one tenth of a millimeter, and rarely over half a millimeter. Its value increases with the angle of incidence, but does not become large enough for accurate measurement until the angle of incidence reaches 65° or 70°. An estimate of the per cent error in measuring a and q gives six for the former, and three for the latter. Since the values of Δ and ψ are proportional to a and q respectively, they will be in error by these same percentages. The formulae

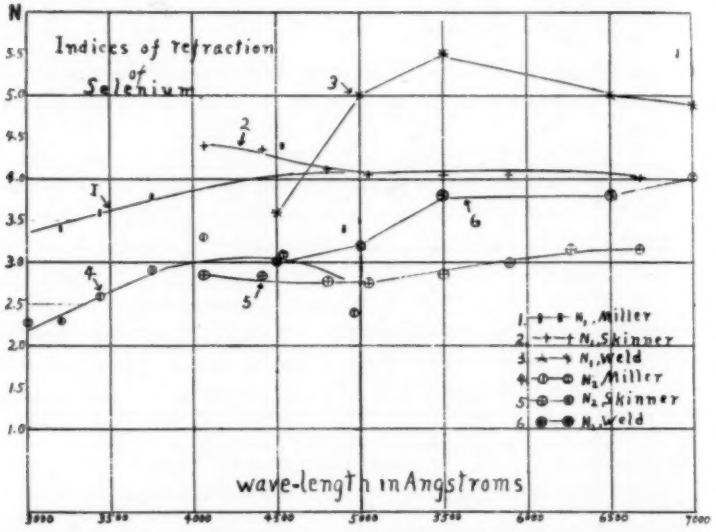

FIG. 4. *Indices of refraction of selenium. Subscripts have the same meaning as in fig. 3.*

for the optical constants are so complicated that it is difficult to discover what effect errors in the values of Δ and ψ have upon them. The result of a number of test calculations shows that a change of 3° in Δ results in a change of 0.15 in N, and 0.1 in K. A change of 1° in ψ makes a change of approximately 0.1 in N, and 0.1 in K. The corresponding values of R are only slightly affected—about 0.01. We may conclude that a single determination of the optical constants may be in error to the following extent: index of refraction 0.25; absorption coefficient 0.2; reflecting power 0.02. The instrumental errors are not

counted in this estimate, as it is not possible to determine the amount. Since the variations among successive determinations of the optical constants are usually not greater than the values given above, it is believed that the errors due to imperfect adjustments of the apparatus are for the most part quite small. The accuracy is greater in the ultra violet region than for the visible region. The maximum accuracy should be attained at about $\lambda = 3750$ Angstroms for the apparatus used, because of the clear sharp spots, and fair values of a and q. By replacing the quartz wedges used by others of proper design, the apparatus could be used satisfactorily throughout the visible spectrum.

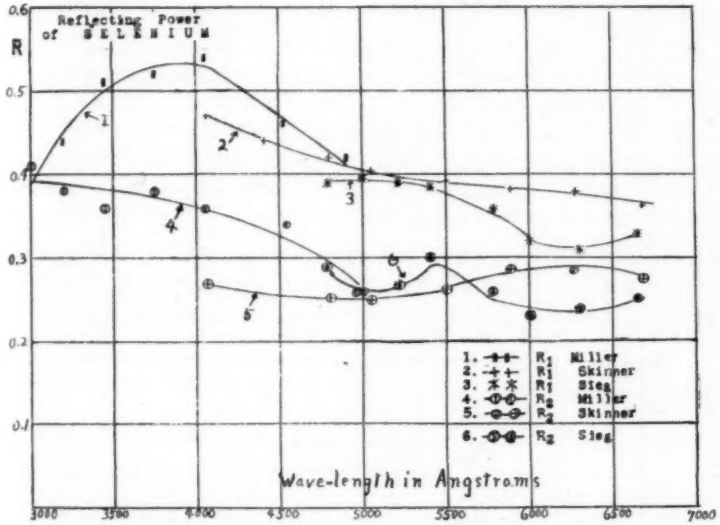

FIG. 5. *Reflecting powers of selenium. The subscripts have the same meaning as in fig 4.*

It is believed that the values of the indices of refraction and reflecting powers of both substances, and the coefficients of absorption of tellurium are correct within 5 per cent on an average. The constants for tellurium are more reliable than those for selenium, due to increased skill in handling the apparatus. The values of the coefficients of absorption of selenium show large variations and may be in error by ten to twenty per cent.

VI. COMPARISON WITH THE WORK OF OTHERS

A comparison of the values obtained by the writer and by several other investigators leads to the following conclusions: (See Figs. 3-8).

Skinner's (loc. cit.[4]) results are the most consistent and probably the most accurate yet obtained for a single crystal of selenium. W. Meier's[11] results are in good agreement with Skinner's values for the vertical position. Meier used the same method as the one here presented,

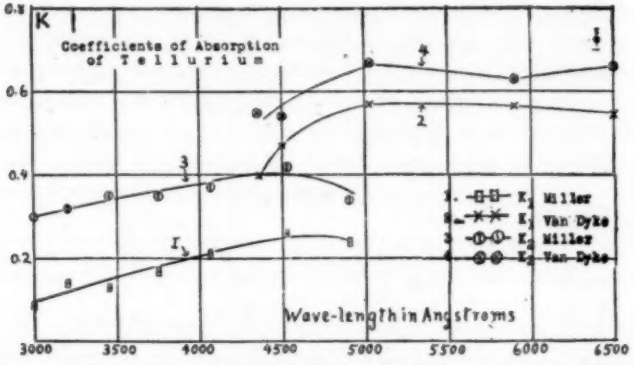

FIG. 6. *Coefficients of absorption of tellurium, as found by two investigators. The subscripts (1) and (2) refer to the parallel and the perpendicular position of the crystal respectively.*

but the selenium used was a cast plate. As pointed out by Sieg (loc. cit.[10], p. 460) the crystals in this case are likely to stand end on at the surface, so that the optical constants obtained should be nearer to the

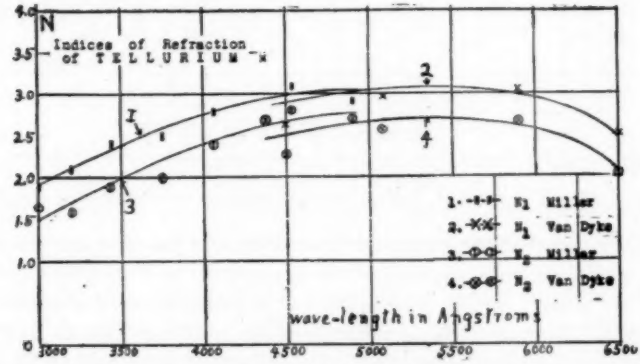

FIG. 7. *Indices of refraction of tellurium. Subscripts have the same meaning as in fig. 6.*

values for the vertical position (axis perpendicular to the plane of incidence) of the crystal. Hulburt's[12] and Sieg's (loc. cit.[10] p. 459)

[11] W. Meier: Ann. der Phys. *31*, p. 1017; 1910.
[12] Hulburt: Astrophys. Jour. *42*, p. 222, 1915.

results on reflecting power agree well with those of Meier within the range measured, and this fact lends additional support to the validity of Skinner's work. Weld's measurements (calculated by Sieg, loc. cit.[10] p. 456) are doubtful, as only one angle of incidence was used (60)°, and at this angle the shift a is too small to be measured with accuracy, especially when the spots are large. My values of the optical constants are in fair agreement with those of Skinner, Meier, Sieg and Hulburt, wherever the determinations overlap. In case of tellurium my values agree fairly well with those of Van Dyke (loc. cit.[6] p. 917) and Sieg,[13] and the consistency of the various measurements is better than for selenium.

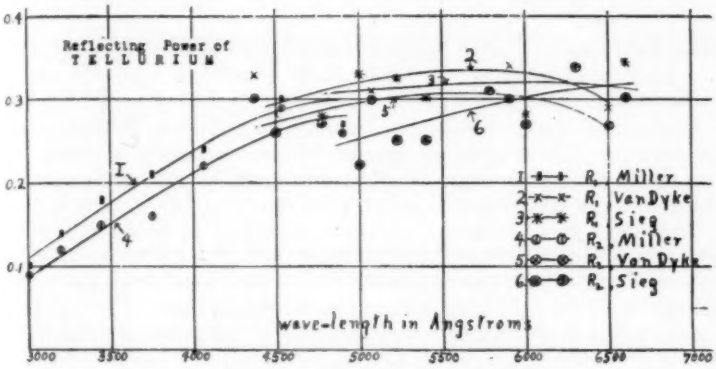

FIG. 8. *Reflecting powers of tellurium.*

VII. CONCLUSIONS

1. The optical constants of isolated crystals of selenium and tellurium have been obtained for wave-lengths from 3000 to 4300 Angstroms for the first time.

2. The region of maximum accuracy for the particular apparatus used is from 3500 to 4000 Angstroms.

3. Both selenium and tellurium have two sets of optical constants. The index of refraction and reflecting power for each substance are greater for the parallel than for the perpendicular position. The reverse is true of the coefficient of absorption of tellurium. The coefficients of absorption of selenium show wide variations for different parts of the spectrum, but average about the same for the two positions of the crystal.

[13] Sieg: J.O.S.A. & R.S.I., 7, p. 147; 1923.

4. There is fair agreement between the values obtained in the visible spectrum with those of other investigators.

5. The extension of the measurements farther into the ultra violet was prevented by absorption of light in the optical apparatus, and by low reflecting power of the crystals for short waves.

The writer wishes to thank the members of the staff of the Physics Department for their interest and help, and especially Professor L. P. Sieg for suggesting the problem and for many helpful suggestions and criticisms during the progress of the work.

UNIVERSITY OF IOWA,
IOWA CITY, IOWA,
DECEMBER 1924.

Classified List of Published Bibliographies in Physics 1910-1922. —By Karl K. Darrow. Pp. 102. $2.00. National Research Council Bulletin, No. 47, July, 1924.

The scope of this publication is indicated by the following brief description. About 3000 classified references are given to books and articles in scientific journals. The list includes all publications on physics in the stated period which give numerous references and also articles that give but few where the references comprise a complete bibliography of a definite subject. Important sources of reference published prior to 1910 are included. With the references is given some indication of the relative value of the bibliographies. The system of classification divides the subject into about 75 heads and 400 sub-heads. A rather brief subject index, six pages, follows the list of references. There is also a list of the 63 periodicals searched.

The classification system is novel in that no attempt is made to divide the subject matter into the customary major divisions of classical physics. A little inconvenience will probably be experienced at first in locating a subject under one of the seventy-five heads given, and the index is too brief to be of much assistance. The difficulty is, however, inherent in the trend of modern physics which has little regard for the obsolete division into mechanics, optics, electricity, etc. The author modestly refrained from proposing a new classification though he would be well qualified to lead the way.

This publication should prove a very useful one and it appears at an opportune time. It will be evident from the above remarks that while the references were compiled primarily as a catalogue of bibliographies they comprise a convenient list of the more important publications on all subjects. It is safe to predict that the book will be frequently used (or rather misused) for this end though the author gives no guarantee that it will fulfill this purpose.

The task of compiling such a volume is an onerous one and all workers in the field of physics will be indebted to Dr. Darrow for his efforts.

F. L. MOHLER

CHROMATIC VISIBILITY COEFFICIENTS BY THE METHOD OF LEAST SQUARES

By Deane B. Judd

Probably the most fundamental set of data relating to color vision is that embodied in the three-color excitation curves (Fig. 1) which represents the laws of three-color mixture.[1] Certainly the most basic of all information regarding visual response, whether it be chromatic or not, is the so-called visibility function which expresses reciprocally

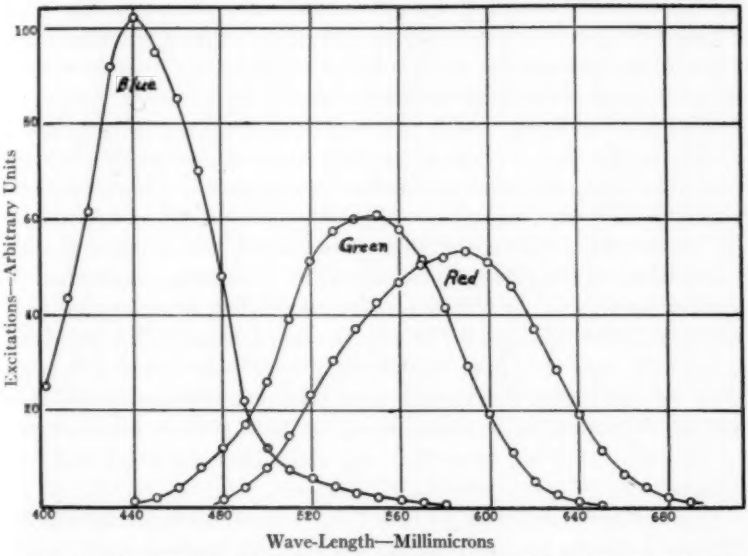

Fig. 1. *The magnitude of the elementary excitations as a function of the wave-length. Data from which the curves were plotted were taken from Report of Committee on Colorimetry 1920-21, J.O.S.A. & R.S.I., 6, p. 548, 1922. The exact values of the ordinates have been recorded in Table 2.*

the intensities of radiant energy of different wave-lengths required to match a standard brilliance. Of the many determinations made of this function, the average normal visibility values, adopted as standard by

[1] Troland, L. T., Colorimetry Report 1920-21, J.O.S.A. & R.S.I., *6*, p. 548; 1922. This data was used to plot the curves of Fig. 1, and subsequently as the basis for the calculation of the visibility coefficients by the method of least squares. See Table 1.

the Illuminating Engineering Society and the Optical Society of America,[2] will be taken as most truly representative (Fig. 2, visibility function, also fifth column, Table 1).

It has long been recognized that, assuming accurate values for the visibility function, satisfactory excitation curves would have to meet the condition of summing to this visibility function when multiplied by factors expressing relative powers of the excitations to generate brilliance. The original form of Koenig's excitation curve was objected to by Ives,[3] on the ground that no possible coefficients would yield even an approximate visibility curve, and he proposes changes to remedy the defect as does also Exner[4] in a more recent article.

The three excitation curves of Fig. 1, then, embodying careful results by Koenig and Dieterici, the above-mentioned defect having been eliminated by the proper choice of reference points, must also yield, when properly weighted by the true luminosity coefficients, a close approximation of the visibility function of Fig. 2.

The question arises, then, what are the true chromatic visibility coefficients for the curves as presented? Troland presents in the same report[5] an account of an experimental determination of the chromatic visibility coefficients using three subjects, resulting in the average values for the coefficients of *R*-0.370; *G*-0.617; and *B*-0.012; but discounts the validity of the results by stating that the subjects varied widely among themselves. In addition to this disquieting assertion, we must add the further fact that the excitations, when weighted by the above factors although the approximation to the visibility function is fairly close, summate to a curve whose maximum is at 550 mμ rather than 556 mμ, indicating rather definitely that the coefficient for the green excitation (0.617) is somewhat larger than the one giving the best agreement.

The method employed by Ives[6] in evaluating these coefficients directly from the two sets of data involved, (a method which yields him the chromatic visibility coefficients referring to Koenig's Modified Fundamental Sensation Curves of *R*-0.568; *G*-0.426; and *B*-0.006) is

[2] Jour. Opt. Soc. of America, *4*, p. 58, 1920. These data may also be found in the report cited above, p. 541.

[3] Ives, H. E., The transformation of Color Mixture Equations, J. Franklin Inst., *180*, p. 673-701, 1915.

[4] Exner, Wien, Berlin, p. 7, 1921.

[5] Loc. cit., pp. 550-551.

[6] Ives, H. E., J. Franklin Inst., *195*, p. 23-44, 1923.

to evaluate the following three relations from any three wave-lengths taken at random from the spectrum, and to solve for the three unknowns:

$$K_1R + K_2G + K_3B = L$$
$$K_1R' + K_2G' + K_3B' = L'$$
$$K_1R'' + K_2G'' + K_3B'' = L''$$

where L, L', and L'' are the visibility values corresponding to his randomly selected wave-lengths; the R, G and B are the ordinates for the three excitations for the same wave-lengths, and K_1, K_2, and K_3 are the coefficients, or unknowns, to be evaluated.

Such a procedure may be quite patently repeated, using different wave-lengths and combinations of wave-lengths, and the solution will yield (unless the experimental results embodied in the two sets of data are absolutely in perfect congruence) a different set of values for the coefficients with each solution. Ives repeated his calculations (described minutely in his 1915 paper) for three sets of three wave-lengths, and averaged his solved values as the true chromatic visibility coefficients.

In the present paper, the true coefficients are assumed to be those values which when used to weight the excitation curves will cause them to summate to an approximate visibility function, the sum of the squares of whose errors from the accepted visibility function shall be a minimum. This applies the familiar principle of Least Squares to the problem of fitting coefficients to the excitation curves that will most accurately harmonize them with the visibility data.

The mathematical analysis leading to the discovery of the coefficients which yield errors, the sum of whose squares is a minimum, is straight-forward:

In the first place, the relation to be satisfied for each wave-length in the visible spectrum is:

$$K_1R + K_2G + K_3B = L$$

where the various K's are the unknown constants; R, G, and B are evaluated for each wave-length by the excitation curves; and L is the visibility for that wave-length.

[7] Another possible solution to this problem of harmonizing the two sets of data is suggested in a recent article by Froelich who develops a formula for purity that does not involve the ascribing of approximate luminosity values to the three primaries with the resulting warping of the visibility function. Her assumptions amount to a distortion of the excitation curves themselves, leaving the more firmly established visibility function intact. See Froelich, Clara L. "Algebraic Methods for the Calculation of Color Mixture Transformation Diagrams." J.O.S.A. & R.S.I., *9*, No. 1, pp. 39-41, 1924.

This relation, however, will not, in general, be exactly satisfied; but the values of K_1, K_2, and K_3 that will make the sum of the squares of the differences between the two sides of the above equation a minimum, are being sought; or, in symbols, the condition to be imposed is that:

$$\Sigma(K_1R+K_2G+K_3B-L)^2 = \text{a minimum.}$$

This is equivalent to the imposition of the three following conditions obtained by the partial differentiation of the above function with respect to the three variables in turn, K_1, K_2, and K_3.

$$\sum\frac{\partial}{\partial K_1}(K_1R+K_2G+K_3B-L)^2=0$$

$$\sum\frac{\partial}{\partial K_2}(K_1R+K_2G+K_3B-L)^2=0$$

$$\sum\frac{\partial}{\partial K_3}(K_1R+K_2G+K_3B-L)^2=0$$

or, performing the indicated steps,

$$2\,\Sigma(K_1R+K_2G+K_3B-L)R=0$$
$$2\,\Sigma(K_1R+K_2G+K_3B-L)G=0$$
$$2\,\Sigma(K_1RK_2G+K_3B-L)B=0$$

and, expanding the indicated products:

$$K_1\,\Sigma RR+K_2\,\Sigma RG+K_3\,\Sigma RB=\Sigma RL$$
$$K_1\,\Sigma RG+K_2\,\Sigma GG+K_3\,\Sigma GB=\Sigma GL$$
$$K_1\,\Sigma RB+K_2\,\Sigma GB+K_3\,\Sigma BB=\Sigma BL$$

This yields three equations of which all quantities except the three K's (K_1, K_2, and K_3, the chromatic visibility coefficients referring to the red, the green, and the blue excitations respectively) can be evaluated from one or the other of the two sets of data that are under the process of coördination. The indicated products have been carried out for intervals of 10mμ along the wave-length scale, and the summation for these intervals over the whole range made. (See Table 1 for the details of this calculation.)

The relations as evaluated by this computation are:

$$2298\,K_1+1964\,K_2+\ 92\,K_3=3926$$
$$1964\,K_1+2518\,K_2+\ 373\,K_3=4203$$
$$\ 92\,K_1+\ 373\,K_2+4903\,K_3=\ 516$$

The form of computation (Gauss' Method) by means of which the solution of these equations was carried out not only rendered the evalu-

TABLE 1. *To evaluate the sums of the squares and the cross-products indicated by the Least Square Analysis. Columns 2, 3, and 4 (Headed R, G, and B, respectively) are the ordinates of the color excitation curves for the specified wave-length of column one as given by Troland (Loc. cit.), and column 5 (Headed L) evaluates the I.E.S. Visibility Function. The remaining columns are filled in with the squares and cross-products as indicated.*

Wave Length mμ	*R*	*G*	*B*	*L*	*RR*	*RG*	*RB*	*RL*	*GG*	*GB*	*GL*	*BB*	*BL*
400	0	0	25	0	0	0	0	0	0	0	0	625	0
10	0	0	43	0	0	0	0	0	0	0	0	1849	0
20	0	0	61	0	0	0	0	0	0	0	0	3721	0
30	0	0	92	1	0	0	0	0	0	0	0	8464	92
40	0	1	102	2	0	0	0	0	1	102	2	10404	204
450	0	2	95	4	0	0	0	0	4	190	8	9025	380
60	0	4	84	6	0	0	0	0	16	336	24	7056	504
70	0	8	70	9	0	0	0	0	64	560	72	4900	630
80	1	12	47	14	1	12	47	14	144	564	168	2209	658
90	4	17	22	21	16	68	88	84	289	374	357	484	462
500	8	26	12	32	64	208	96	256	676	312	832	144	384
10	15	39	9	48	225	585	135	720	1521	351	1872	81	432
20	23	51	6	67	529	1173	138	1541	2601	306	3417	36	402
30	31	57	4	84	961	1767	124	2604	3249	228	4788	16	336
40	37	60	3	94	1360	2220	111	3478	3600	180	5640	9	282
550	42	61	2	99	1764	2562	84	4158	3721	122	6039	4	198
60	47	58	1	100	2209	2726	47	4700	3364	58	5800	1	100
70	51	52	1	95	2601	2652	51	4845	2704	52	4940	1	95
80	52	42	0	87	2704	2184	0	4524	1764	0	3654	0	0
90	54	30	0	76	2916	1620	0	4104	900	0	2280	0	0
600	51	20	0	63	2601	1020	0	3213	400	0	1260	0	0
10	46	11	0	50	2116	506	0	2300	121	0	550	0	0
20	38	6	0	38	1444	228	0	1444	36	0	228	0	0
30	29	3	0	26	841	87	0	754	9	0	78	0	0
40	20	1	0	17	400	20	0	340	1	0	17	0	0
650	12	0	0	10	144	0	0	120	0	0	0	0	0
60	7	0	0	6	49	0	0	42	0	0	0	0	0
70	4	0	0	3	16	0	0	12	0	0	0	0	0
80	2	0	0	2	4	0	0	4	0	0	0	0	0
90	3	0	0	1	9	0	0	3	0	0	0	0	0
Totals.....					22983	19638	921	39260	25185	3735	42026	49029	5159

From these totals are built up the equations (See text) whose solution yields the values of the chromatic visibility coefficients.

ation of the constants easy and accurate (because of the check maintained after each step) but also made available the quick calculation of their probable errors.[8]

The values resulting from the solution of these equations are:

K_1 (Red Excitation) = .8481 ± .0360
K_2 (Green Excitation) = 1.0062 ± .0333
K_3 (Blue Excitation) = .01290 ± .01431

These coefficients, then, are the weights which when applied to the excitation curves of Fig. 1, make them summate to the closest approximation of the visibility function of Fig. 2. (Fig. 2 also shows the

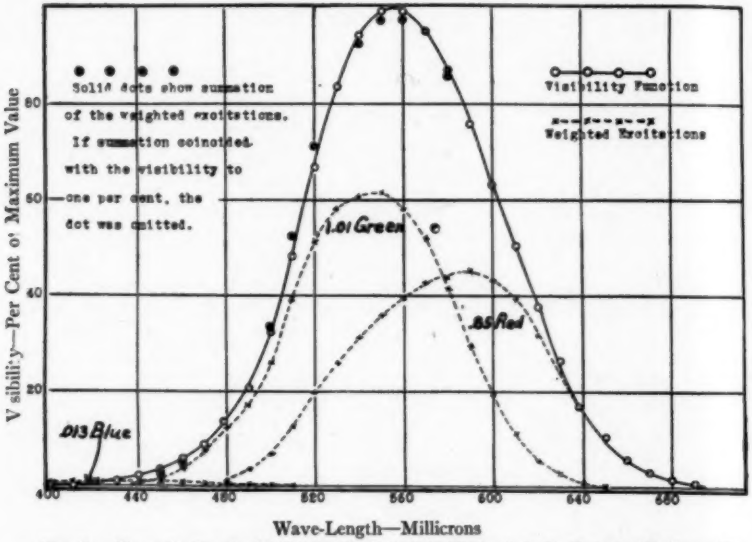

FIG. 2. *Shows the Standard I.E.S. and O.S.A. (See Troland, L. T., Report of the Committee on Colorimetry for 1920-21, J.O.S.A. & R.S.I., 6, p. 541, 1922.) Visibility Function together with the elementary color excitations weighted according to their brightness-producing powers by the coefficients herein derived. The sum of the weighted excitations is seen to approximate the visibility function.*

weighted excitations and the summation points that do not exactly coincide with the accepted visibility function.) In order to show in the conventional fashion just how close the correspondence is between the weighted excitation sums and the accepted I. E. S. Visibility Function, Table 2 has been compiled.

[8] Merriman's Method of Least Squares, Third Edit., pp. 82-85, 1911.

TABLE 2. *Comparison of the visibilities as calculated from the color excitation curves weighted by the Least Square Coefficients with the accepted I.E.S. Visibility Function.*

Wave Length mμ 1	Excitations			Products by the Coefficients			Some of the Products (Calculated visibility) 8	I.E.S. Visibility 9	Diff. (v) 10	Square of Diff. (v^2) 11
	Red 2	Green 3	Blue 4	.848 5	1.006 6	.0129 7				
400	0	0	25.3	0	0	0.3	0.3	0.04	+0.3	.09
10	0	0	43.3	0	0	0.6	0.6	0.12	+0.5	.25
20	0	0	61.4	0	0	0.8	0.8	0.40	+0.4	.16
30	0	0	91.5	0	0	1.2	1.2	1.16	0.0	.00
40	0	0.7	101.9	0	0.7	1.3	2.0	2.3	−0.3	.09
450	0	1.6	95.0	0	1.6	1.2	2.8	3.8	−1.0	1.00
60	0	3.8	84.2	0	3.8	1.1	4.9	6.0	−1.1	1.21
70	0	8.1	69.7	0	8.1	0.9	9.0	9.1	−0.1	.01
80	1.4	12.2	47.3	1.2	12.3	0.6	14.1	13.9	+0.2	.04
90	4.1	16.9	22.0	3.5	17.0	0.3	20.8	20.8	0.0	.00
500	8.3	26.0	12.3	7.0	26.2	0.2	33.4	32.3	+1.1	1.21
10	15.1	39.1	8.7	12.8	39.3	0.1	52.2	48.4	+3.8	14.44
20	23.3	51.0	6.1	19.8	51.3	0.1	71.2	67.0	+4.2	17.64
30	30.7	57.2	4.3	26.0	57.5	0.1	83.6	83.6	0.0	.00
40	37.3	60.3	2.9	31.6	60.7	0	92.3	94.2	−1.9	3.61
550	42.4	61.2	1.8	36.0	61.6	0	97.6	99.3	−1.7	2.89
60	46.6	57.8	1.1	39.5	58.2	0	97.7	99.6	−1.9	3.61
70	50.5	51.7	0.7	42.8	52.0	0	94.8	95.2	−0.4	.16
80	52.0	41.5	0.4	44.1	41.7	0	85.8	87.0	−1.2	1.44
90	53.5	29.6	0	45.4	29.8	0	75.2	75.7	−0.5	.25
600	51.0	19.6	0	43.2	19.7	0	62.9	63.1	−0.2	.04
10	46.2	11.3	0	39.2	11.4	0	50.6	50.3	+0.3	.09
20	37.5	5.9	0	31.8	5.9	0	37.7	38.0	−0.3	.09
30	28.5	2.9	0	24.2	2.9	0	27.1	26.2	+0.9	.81
40	19.5	1.0	0	16.5	1.0	0	17.5	17.0	+0.5	.25
650	11.8	0.3	0	10.0	0.3	0	10.3	10.3	0.0	.00
60	6.8	0	0	5.8	0	0	5.8	5.9	−0.1	.01
70	4.0	0	0	3.4	0	0	3.4	3.0	+0.4	.16
80	2.2	0	0	1.9	0	0	1.9	1.6	+0.3	.09
90	1.1	0	0	0.9	0	0	0.9	0.8	+0.1	.01
									Total	49.65

Probable Error of any single calculated visibility $= r = .6745\sqrt{\frac{\Sigma pv^2}{n-q}}$

$$r = .6745\sqrt{\frac{49.65}{27}} = 0.914$$

The first column gives the wave-length in millimicrons; the second, third and fourth, the magnitude of the three excitation curves[9] for the indicated wave-lengths; and the fifth, sixth and seventh, those magnitudes weighted by the coefficients just derived. Column eight is the sum of the three preceding columns and should equal the I.E.S. Visibility Function as it appears in column nine. Just how closely does column eight check with column nine may be seen by referring to column ten, the difference between the two. The changes from plus to minus in this column indicate that the calculated curve crosses the accepted function eight times. Column eleven is made up of the squares of the differences recorded in column ten and its sum is used as Σpv^2 in the determination of the probable error between the calculated and accepted visibilities, making use of the following formula:

$$r = .6745\sqrt{\Sigma pv^2/(n-q)}$$

where: r = probable error of any single calculated visibility compared to the accepted visibility.

p = weight of each individual observation, taken as unity for each case in this computation, on the assumption that the data for all wave-lengths are equally well determined.

v = difference between the calculated and the accepted visibility for each wave-length.

n = number of observations taken. (Since 10 mμ intervals were chosen, the total number in this computation was $700-400/10=30$).

q = number of derived constants = 3.

Thus the sum of column eleven is equal to Σpv^2 and:

$$r = .6745\sqrt{49.65/27} = 0.914 .$$

Thus the probable error between the calculated visibilities and the accepted visibilities appears as less than one per cent. The values for visibility as calculated from the excitations using Troland's experimental coefficients and compared in the same fashion with the accepted visibility yield a probable error of 2.07, or a little greater than two per cent, the amount of error thus being more than doubled over that which is inevitably introduced (0.914) through the essential disagreement inherent because of error in the two sets of data themselves.

To compare the above listed coefficients directly with Troland's Experimental Values, it is necessary to reduce them proportionately until their sum is unity. The reduction, together with similar changes

[9] These are the values as taken from the Colorimetry Committee's Report for 1920-21 as before referred to. Cf. Troland, L. T., J.O.S.A. & R.S.I., *6*, p. 548, 1922.

in the probable errors, yields the following values for relative chromatic visibility coefficients:

		Troland's Experimental Values
Red.....	.455±.019	.370
Green.....	.538±.018	.617
Blue.....	.00691±.00767	.012

It will be immediately noted that the outstanding defect of Troland's values (as already pointed out, the overweighting of the green excitation's power to generate brilliance) has been remedied in the right direction. That the magnitude of the correction checks also may be noted from the fact that the visibility curve by summation has its maximum at the same place as the accepted experimental function (See Fig. 2), namely: at 556mμ.

CHROMATIC VISIBILITY COEFFICIENTS USED IN BRIGHTNESS CALCULATIONS

In transferring from the tri-chromatic system of color notation in which the red, green and blue excitation totals completely specify the stimulus value of the light beam, to the monochromatic system in which dominant wave-length, purity and brightness are the units of specification the relative brightnesses of two or more beams may be directly calculated by taking the sum of the excitation totals after they have been weighted by the chromatic visibility coefficients. In order that the magnitude of the error introduced in such a calculation by the use of Troland's coefficients instead of the more consistent values above-calculated, the brightnesses of a set of papers[10] illuminated by an equal energy spectrum have been calculated in three different ways: (1) by Troland's coefficients; (2) by the Least Square Coefficients; and, (3) by a theoretically rigorous graphical method against whose results the first two sets of figures are checked.

In the first column of the above described table (Table 3) is the color name by which an observer of the papers would normally characterize its hue by daylight. This serves to distinguish roughly between the papers.

The second column is made up of the brightness of these papers as calculated by the following graphical method:

1. The reflection coefficients of the paper for each wave-length (10 mμ intervals) throughout the spectrum (400 to 700 mμ) were

[10] Judd, D. B., "Spectral Energy Distributions Produced by Rotary Mixing of Complementary Papers," J.O.S.A. & R.S.I., *9*, p. 98, 1924.

multiplied by the visibility for the corresponding wave-length. This evaluates (RL).

2. A curve was plotted of the above products as ordinates against the wave-length as abscissa, the smoothing between plotted points giving $(RL)=f(\lambda)$

TABLE 3. *Use of the chromatic visibility coefficients in brightness calculations. With equal energy spectrum as the white reference point, the following two sets of coefficients were used:*

	Troland's Experimental Coefficients	Least Square Coefficients
Red	.366	.449
Green	.624	.545
Blue	.010	.0058

Color Name	Brightness Planimeter	Troland's Coefficients		Least Square Coefficients		
		Brightness	Error	Brightness	Error	Diff.
1	2	3	4	5	6	7
Red	13.5	12.1	−1.4	13.0	−0.5	+0.9
Red	20.0	18.6	−1.4	20.2	+0.2	+1.6
Red Orange	29.5	27.1	−2.4	29.1	−0.4	+2.0
Orange	43.8	42.5	−1.3	45.1	+1.3	+2.6
Yellow	70.6	69.9	−0.7	71.9	+1.3	+2.0
Yellow	83.0	83.5	+0.5	85.7	+2.7	+2.2
Yellow	89.2	86.6	−2.6	88.5	−0.7	+1.9
Yellow Green	69.6	71.0	+1.4	71.0	+1.4	0.0
Green	40.2	41.7	+1.5	41.0	+0.8	−0.7
Blue Green	42.9	43.3	+0.4	42.7	−0.2	−0.6
Green Blue	24.9	26.8	+1.9	25.6	+0.7	−1.2
Blue	15.5	14.4	−1.1	13.1	−2.4	−1.3
Blue Violet	11.5	11.9	+0.4	11.0	−0.5	−0.9
Violet	14.8	15.1	+0.3	14.7	−0.1	−0.4
Violet Red	20.8	21.1	+0.3	21.6	+0.8	+0.5
Black	4.9	4.8	−0.1	5.0	+0.1	+0.2
White	100.0	100.0	0.0	100.0	0.0	0.0
		I Average	.07	Average	0.88	1.2

3. The area of this curve (between the curve and the x-axis) was measured in square inches by means of a planimeter.

$$A=\int_{400}^{700} RLd\lambda$$

4. The resulting number of square inches was divided by 1/100 of the number of square inches beneath the visibility function (multiplied

by a reflection coefficient of 1.00, the reflection due to a non-selective surface arbitrarily chosen as white and against which all reflection measurements were made). This quotient represents the per cent brightness of the paper in question, the above-referred-to standard white being 100 per cent bright. The quotient, therefore, is recorded in the second column headed: "Brightness, planimeter." In symbols the per cent brightness is:

$$\text{Per cent brightness} = \frac{100\int_{400}^{700} RLd\lambda}{\int_{400}^{700} Ld\lambda}$$

Since E is in each case less than unity, from the formula it will be seen that the per cent brightness must of necessity be less than 100.

The third column gives the per cent brightness as calculated from the excitation totals[11] weighted by Troland's experimental chromatic visibility coefficients, considering, as before, the standard white to be one hundred per cent bright.

The fourth column represents the per cent error between the planimeter values for brightness and the brightness by Troland's coefficients; and the entries are obtained by simple subtraction of column two from column three, the algebraic sign of the result being given. The average error is seen to be 1.07 per cent.

The fifth column gives the per cent brightness (corresponding to column three) calculated from the excitation totals by the use of the Least Square Chromatic Visibility Coefficients.

The sixth column, like column four, gives the per cent difference of the results in column five as checked against the planimeter values of column two. The average error, 0.88 per cent, shows a small increase

[11] The excitation totals appear in Table 1 of the article just referred to (Judd, J.O.S.A. & R.S.I., *9*, No. 2, p. 98, 1924), but the quoted excitation totals lack a little in the red total and considerable in the blue total since they refer to noon sunlight instead of equal energy illumination. The only reason equal energy spectrum illumination was chosen in this case is on account of the fact that the original carefully made planimeter readings, against which the other two sets of results are checked, refer to equal energy and not noon sunlight.

Through similar considerations, this change in point of reference for white (from average noon sunlight to equal energy spectrum) causes a slight change in the values for the chromatic visibility coefficients, as follows:

	Troland's Experimental Coefficients		Least Square Coefficients	
	Sunlight	Equal Energy	Sunlight	Equal Energy
Red.....	.370	.366	.455	.449
Green.....	.617	.624	.538	.545
Blue.....	.012	.010	.0069	.0058

in accuracy (compare 0.88 per cent with 1.07 per cent) due to the use of the most consistent coefficients.

The entries in the seventh column represent the changes in per cent brightness introduced by substituting the least square coefficients (.449; .545; .0058) for the Troland Values (.336; .624; .010). The regular shift from plus changes to negative changes is, of course, easily accounted for. It is to be noticed that the average difference in per cent brightness is 1.2 per cent, or about one-eighth the change introduced in the red and green (8.3 per cent and 7.9 per cent respectively) chromatic visibility coefficients.

This affords an explanation of the difficulty of checking the visibility coefficients by experimenting with subjects making a brilliance discrimination. Errors made in judging brightness (and they are inevitable and fairly large) are seen to be multiplied by six or eight when the measurements are made to refer to the chromatic visibility coefficients themselves.

The reason for the surprisingly small change in brightness corresponding to a marked change in the red and green visibility coefficients can be pointed out easily by referring to the excitation curves themselves (Fig. 1). It is seen that the red and green excitation curves overlap each other to a great extent, so that a loss in weight of one coefficient with a resulting gain in the other affects the total brightness only for distributions of energy that slope sharply through the center of the red-green area (about 600 to 560 mμ) corresponding to the narrow region from orange-yellow to yellow-green, and not in marked degree for those. In this connection it is to be noted that the largest differences recorded in column seven of Table 3 are from the Red-Orange to the Yellow-Green. However, even for these pigment colors which have saturations approaching the highest obtainable in pigments or colored papers, and which would therefore yield the largest errors, the errors are seen to be less than 3 per cent.

On account of the small errors (about 1.2 per cent) in brightness yielded by rather large errors (about 8 per cent) in the Chromatic Visibility Coefficients themselves, it seems useless to write the coefficients to the scale of one thousand, as has hitherto been customary, the rounder figures: R-0.45; G-0.54 and B-0.01; being easier to deal with as well as having just as much significance in ordinary brightness calculations such as those in Table 3. The above round figures lie within the probable errors as calculated: $R-0.455\pm.019$; $G-0.538\pm.018$; $B-0.00691\pm.00767$.

SUMMARY

1. A straight-forward method for the fitting of chromatic visibility coefficients to any set of excitations that may summate to any chosen visibility function is presented.

2. Choosing the modified Koenig-Dieterici Fundamental Excitations, as given in the Report of the Colorimetry Committee for 1920-21, to summate to the standard I.E.S. and O.S.A. Visibility Function, the following chromatic visibility coefficients were derived: $R-0.455 \pm .019$; $G-0.538 \pm .018$; $B-0.00691 \pm .00767$.

3. By a specific set of representative calculations for the brightness of ordinary pigment colors the needlessness of stating the coefficients to three places is shown and the following approximate coefficients proposed for this sort of work: $R-0.45$; $G-0.54$; $B-0.01$.

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APPENDIX

Since the completion of the just-described calculation for the Chromatic Visibility Coefficients, the visibility data of Gibson and Tyndall[12] has become available, and the desirability of carrying out the same calculation with respect to the results of this authoritative work has been pointed out by Dr. Herbert E. Ives. Accordingly, then, using the same color excitation curves (as given by Troland in the Report of the Colorimetry Committee for 1921), to summate to the average results of Gibson and Tyndall, the following normal equations (for method of computation see Table 1 in the text) were computed:

$$2298\,K_1+1964\,K_2+\ 92\,K_3=3972$$
$$1964\,K_1+2518\,K_2+\ 373\,K_3=4279$$
$$\ 92\,K_1+\ 373\,K_2+4903\,K_3=\ 606$$

These equations are almost identical with those yielded by the previous calculation (See page 638), and show how very closely the two visibility functions coincide; indeed the only difference is a slight increase in the violet and the green regions of the spectrum.

The values of the coefficients which will satisfy the above set of equations, together with the probable errors calculated as before, are: K_1 (Red Excitation) $-0.835 \pm .029$; K_2 (Green Excitation) $-1.044 \pm .027$; K_3 (Blue Excitation) $-0.0288 \pm .0115$.

Reducing these values as before so that their sum is unity, we have: $R-0.438 \pm .015$; $G-0.547 \pm .014$; $B-0.0151 \pm .0060$. (These results

[12] Gibson and Tyndall, Sci. Paper of Bur. Stds., No. 475, *19*, p. 154, 1923.

are, as might be expected, slightly larger for the green and blue coefficients.)

It is to be noted that the approximate coefficients for use in brightness determinations of ordinary pigment colors as previously proposed, viz.: $R-0.45$; $G-0.54$; $B-0.01$; still lie within the probable errors of the results from the Gibson-Tyndall visibility data.

Worthy of mention at this point is the distinct gain in correspondence of the weighted excitation sum with the Gibson-Tyndall visibility function as compared to that obtained when the I.E.S. Standard Visibility Function and the I.E.S. Least Square Coefficients were used. In order to make easy the comparison, Table 4, drawn up so as to be exactly similar to Table 2, has been compiled. As before, column eight represents the weighted excitation sums, column nine the observed visibilities, and column ten the difference between the two.

The sum of the squares of these errors (column eleven, Table 4) of the weighted excitation sums against the Gibson-Tyndall Visibility Function is calculated as 35.39. The probable error of any single excitation sum is given by:

$$r = .6745\sqrt{\Sigma pv^2/n-q} = .6745\sqrt{35.39/27} = 0.772 \text{ per cent}$$

This probable error is distinctly smaller than that found for the I.E.S. Visibility Function with its least square coefficients ($r = 0.914$ per cent) and is much smaller than the probable error resulting from the use of Troland's Experimental Coefficients applied o the I.E.S. Visibility Function ($r = 2.07$ per cent).

That the exact manner may be made plain in which the Gibson-Tyndall visibility data is more consistent with the color excitation curves than is the I.E.S. data, Fig. 3 has been included. This figure shows the visibility plotted on a magnified scale against the wave-length so that the rather small errors may be made readable. Both the I.E.S. and the Gibson-Tyndall visibilities together with their respective approximation from the color data are shown. The wave-lengths higher than 600 mμ have not been included because the agreement, not only between the I.E.S. and the Gibson-Tyndall data, but also between their weighted-excitation-sum approximations is excellent for those wave-lengths.

If attention is confined for the moment to the I.E.S. Visibility Function and the excitation sums as weighted by the coefficients derived from that function it will be seen that (disregarding many minor ir-

TABLE 4. *Comparison of the visibilities as calculated from the color excitation curves weighted by the least square coefficients and the average weighted results of Gibson and Tyndall.*

Wave Length mμ 1	Excitations			Products by the Coefficients			Sum of the Products (Calculated visibility)	Gibson and Tyndall Visibility	Diff. (v)	Square of diff. (v^2)
	Red 2	Green 3	Blue 4	.835 5	1.044 6	.0287 7	8	9	10	11
400	0	0	25.3	0	0	0.7	0.7	0.5	+0.2	.04
10	0	0	43.3	0	0	1.2	1.2	1.2	0.0	.00
20	0	0	61.4	0	0	1.8	1.8	2.2	−0.4	.16
30	0	0	91.5	0	0	2.6	2.6	3.3	−0.7	.49
40	0	0.7	101.9	0	0.7	2.9	3.6	4.3	−0.7	.49
450	0	1.6	95.0	0	1.7	2.7	4.4	5.1	−0.7	.49
60	0	3.8	84.2	0	4.0	2.4	6.4	6.9	−0.5	.25
70	0	8.1	69.7	0	8.5	2.0	10.5	10.3	+0.2	.04
80	1.4	12.2	47.3	1.2	12.7	1.4	15.3	14.3	+1.0	1.00
90	4.1	16.9	22.0	3.4	17.6	0.6	21.6	19.6	+2.0	4.00
500	8.3	26.0	12.3	6.9	27.2	0.4	34.5	31.8	+2.7	7.29
10	15.1	39.1	8.7	12.6	40.8	0.2	53.6	52.3	+1.3	1.69
20	23.3	51.0	6.1	19.4	53.2	0.2	72.8	73.2	−0.4	.16
30	30.7	57.2	4.3	25.6	59.7	0.1	85.4	87.8	−2.4	5.76
40	37.3	60.3	2.9	31.2	63.0	0.1	94.3	96.4	−2.1	4.41
550	42.4	61.2	1.8	35.4	64.0	0.1	99.5	99.8	−0.3	.09
60	46.6	57.8	1.1	38.9	60.4	0	99.3	99.1	+0.2	.04
70	50.5	51.7	0.7	42.1	54.0	0	96.1	94.7	+1.4	1.96
80	52.0	41.5	0.4	43.4	43.4	0	86.8	86.3	+0.5	.25
90	53.5	29.6	0	44.6	30.9	0	75.5	75.4	+0.1	.01
600	51.0	19.6	0	42.5	20.5	0	63.0	63.4	−0.4	.16
10	46.2	11.3	0	38.6	11.8	0	50.4	51.1	−0.7	.49
20	37.5	5.9	0	31.3	6.2	0	37.5	38.9	−1.4	1.96
30	28.5	2.9	0	23.8	3.0	0	26.8	27.9	−1.1	1.21
40	19.5	1.0	0	16.3	1.0	0	17.3	18.4	−1.1	1.21
650	11.8	0.3	0	9.9	0.3	0	10.2	11.3	−1.1	1.21
60	6.8	0	0	5.7	0	0	5.7	6.4	−0.7	.49
70	4.0	0	0	3.3	0	0	3.3	3.5	−0.2	.04
80	2.2	0	0	1.8	0	0	1.8	1.8	0.0	.00
90	1.1	0	0	0.9	0	0	0.9	0.9	0.0	.00
									Total	35.39

Probable Error of any single calculated visibility $= r = .6745\sqrt{\frac{\Sigma pv^2}{n-q}}$

$r = .6745\sqrt{35.39/27} = 0.772$ per cent

regularities) the weighted-color-curve sums fail to agree with the visibility function in two outstanding particulars, as follows;

1. In the extreme violet where the blue excitation curve is still quite high (See Fig. 1, 400-440 mμ) the I.E.S. Visibility falls almost to zero. This means that any weight given to the blue excitation whatsoever will fail to yield a good approximation: if low, the curve agrees well for 400-420 mμ but sags below in the wave-length interval

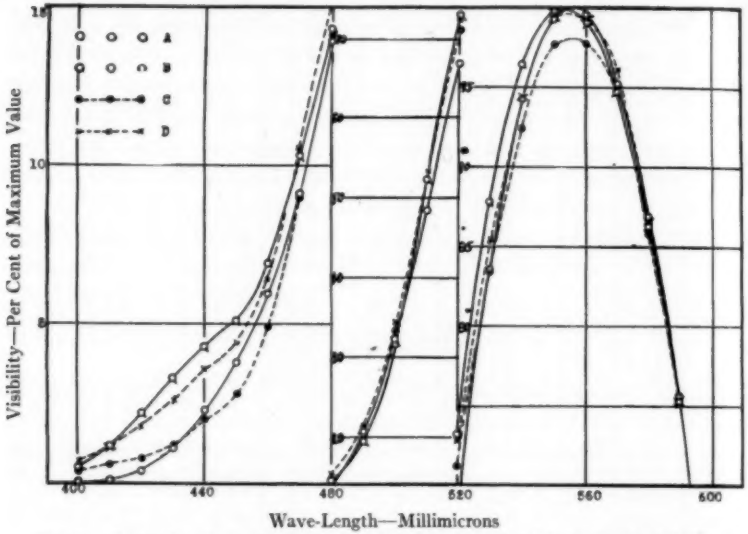

FIG. 3. *Comparing the recent Gibson-Tyndall visibility data with the Standard I.E.S. and O.S.A. visibility. The gain in consistency of the Gibson-Tyndall data with the color excitation sums (dotted curve) is most striking at the point of maximum visibility where the agreement is definitely bettered. A—I.E.S. Visibility; B—Gibson-Tyndall Visibility; C—Weighted Excitation Sum, I.E.S. Coefficients; D—Weighted Excitation Sum, Gibson-Tyndall Coefficients.*

just higher than this; if high, the sum checks fairly well for 430-460 mμ. but rises to six or eight times the value of the visibility for 400-420 mμ, The least square coefficients adjust the excitation sum so that it crosses the I.E.S. visibility at about 430 mμ.

2. Again, in the very maximum of the visibility, the excitation sum is seen to fall short. The reason why no adjustment of weights of the red and green excitations can correct this is that the shape of those excitations (See Fig. 1) is such as to yield a sum that approaches a maximum more bluntly, no matter what the weights, than does the I.E.S. function.

As before mentioned, the Gibson-Tyndall visibility checks very well with the I.E.S. curve, there being but two appreciable changes: (1) An increase in the extreme violet region, and (2) an increase in the green region of the spectrum. Both of these differences tend to correct the outstanding discrepancies between the color and the luminosity data, thus:

1. The bulge in the violet region (See Fig. 3) allows the maximum of the blue excitation to fit much closer. While the differences, themselves, are slightly larger for the Gibson-Tyndall comparison than for the I.E.S., the per cent difference based on the value of the excitation at that wave-length is tremendously smaller as the following tabulation shows:

Wave length mμ	I.E.S. Visibility				Gibson-Tyndall Visibility			
	Obs.	Color Sum	Diff.	Per cent Diff.	Obs.	Color Sum	Diff.	Per cent Diff.
400	0.04	0.33	0.29	725	0.5	0.7	0.2	40.0
410	0.12	0.56	0.44	366	1.2	1.2	0.0	0.0
420	0.40	0.79	0.39	98	2.2	1.8	0.4	18.2
430	1.16	1.18	0.02	2	3.3	2.6	0.7	21.2
440	2.30	2.00	0.30	13	4.3	3.6	0.7	16.3
		Average	0.29	241		Average	0.4	19.0

The error in per cent is seen to fall from 241 per cent to 19.0 per cent.

2. The increase in the green region serves to make the "nose" of the maximum more blunt, with the result that the excitation sums weighted according to the coefficients derived to fit the Gibson-Tyndall data check very closely, as a glance at Fig. 3 will show. The value of the weighted color sums rises to 99.8 per cent as a maximum at 554 mμ. As nearly as can be seen from the curve, the actual maximum of the Gibson-Tyndall Visibility Function is at 553 mμ with a value, of course, of 100.0 per cent. This agreement, which is distinctly better than that yielded by the I.E.S. coefficients (which gives a maximum of only 98.0 per cent) seems satisfactory.

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Theories of the Active Modification of Nitrogen.—Saha and Sur assemble the following facts about the active modification of nitrogen: (a) the absorption-spectrum of ordinary nitrogen consists of a band at wave-lengths corresponding to about 8 volts; (b) active nitrogen excites most if not all of the arc-lines of Na and Mg, both having ionizing-potentials lower than 8 volts; (c) active nitrogen excites many arc-lines of Hg, but not certain lines demanding an excitation potential of 9.4 volts. From these he concludes that active nitrogen consists of nitrogen molecules temporarily in a metastable state of which the potential energy is greater than the normal value by somewhat more than 8 volts. To explain why the afterglow of active nitrogen is bright in slightly contaminated nitrogen and feeble or lacking in very pure nitrogen excited in the same way it is necessary to assume *ad hoc* that the metastable molecules are equally present in both cases, but in the latter case return in one leap to the normal state, producing only radiation in the far ultraviolet; while collisions with other than nitrogen molecules cause them to return in stages, some of which result in visible radiation. Many experiments suggest themselves to test this theory. To this Birge rejoins that the band-spectrum of active nitrogen, containing certain bands identified in the ordinary spectrum of nitrogen and interpreted from that spectrum, shows that before emission the activated nitrogen molecules are chiefly in a certain state characterized by a particular electron-configuration and either 10, 11 or 12 vibrational quanta; this state corresponds to an energy some 11 or 12 volts greater than the normal energy of the molecule, although the band-system has not yet been mapped with sufficient completeness to make sure of the exact value. The rôle of the contaminations, according to Birge, is to absorb the free electrons which if left to fly about would speedily reduce the "activated" molecules to their normal state.—[M. N. Saha and N. K. Sur, Allahabad; Phil. Mag. *48*, pp. 421-428; 1924. R. T. Birge, California; Nature *114*, p. 642; 1924.] KARL K. DARROW

Beta-ray Spectrum of Mesothorium 2.—This is the 89th element and disintegrates into the 90th by emission of a nuclear electron. Many electrons of distinct speeds are emitted, and the question is whether they can be accounted for by assuming that gamma-rays of a few characteristic frequencies come out of the nucleus and expel these electrons from the various orbits. The velocity spectrum of the emitted electrons is mapped in the usual way, 31 velocity-groups of electrons are detected, and 22 of these are attributed to 7 gamma-rays extracting electrons from various K, L, M and N orbits. The 7 gamma-ray frequencies in turn may be correlated by a combination-principle with 5 energy-levels in the nucleus. Whether these numerical agreements are abundant and exact enough to make the stated interpretation not only possible but probable is a very difficult question.—[D. H. Black, Cavendish; Proc. Roy. Soc. *A106*, pp. 632-640; 1924].

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STAGES IN THE EXCITATION OF THE SPECTRA OF CADMIUM[1]

By Arthur E. Ruark and Roy L. Chenault

In the classification of spectra it is helpful to know the voltages at which new groups of lines are excited. Quite often it is safe to assume that all lines which put in an appearance at a given value of the applied potential are emitted by the same type of atom or ion, but this assumption may lead to error. Suppose, for example, that the first ionization potential of an element E is 10 volts and that an electron may be removed from a more closely bound group at 20 volts, while the ionization potential of E^+ is 22 volts. With an applied potential slightly above 22 volts, we have ionization from the 20 volts level of E as the result of a single electron impact,[1] while successive impacts produce E^+ and then E^{++}. Thus we obtain a second stage in the spectrum of the neutral atom, and also the spectrum due to E^+. The relative intensities of these spectra will depend primarily on the probability of double ionization by successive impacts as compared with that of single ionization from the 20 volt level of E. That is, high current densities will strengthen the spectrum of E^+ relative to the 20 volt spectrum of the neutral atom. These considerations show the desirability of including data on current densities in tables giving the appearance voltages of spectrum lines. Data of this kind are here presented for cadmium, which lies on the right side of the second column of the periodic table together with zinc and mercury. Several lines of neutral cadmium are also classified.

We have obtained spectra of cadmium from a three electrode low voltage arc, at applied potentials between 8 and 65 volts. (The actual potentials were smaller.) The discharge tube was so constructed as to make it possible to utilize the light of the arc very efficiently. It was made from a Pyrex tube about one inch in diameter. The central portion of the tube was lined with a cylinder of very thin sheet iron, open at both ends. A tungsten cathode closely surrounded by a helix of nickel wire was supported at the center of this cylinder. The helix and the cylinder were at the same potential, so that the electrons were

* Published by permission of the Director of the Bureau of Standards of the U.S. Department of Commerce.

[1] Impacts of this type have been observed by Mohler and Ruark, J.O.S.A. and R.S.I., 7, p. 819; 1923. At 12.4 volts an electron is removed from a 6_1 orbit of the thallium atom, while the valence electron remains on a 6_2 orbit.

accelerated only by the potential between the cathode and the helix, most of the collisions occurring in the region between the helix and the cylinder. The central portion of the tube was surrounded by an electric furnace. The magnetic field of the heating current caused the electrons to spiral along the tube, increasing their effective path and drawing out the discharge into a long column which could be observed end on. It was possible to work with total currents below 10 milliamperes without unduly lengthening the exposures.

Initial velocity corrections were made by taking current-voltage curves to locate the first ionization potential. The gas pressure was usually less than .0001 mm. Seed 30 plates were used, and all exposures were obtained with a Hilger quartz spectrograph, size E2. All wave lengths are recorded in International Angstroms.

We shall now discuss the appearance voltages of arc lines which have not previously been classified, and of lines belonging to higher spectrum stages. The photographs obtained below the ionization potential (8.96 volts) show that all the stronger lines of the arc spectrum appear at exactly the voltage intervals to be expected from the classification given in Fowler's report on series. This is an experimental proof that the classification is correct in its main features, and requires no further comment. In what follows we shall use the series notation of Paschen for the lines of neutral cadmium. The spectrum of singly ionized cadmium has been classified by von Salis.[2] He uses total quantum numbers as assigned by Bohr for the numeration of spectral terms. We shall follow this system for the lines which he has classified.

Table I records the voltages and currents at which spectral lines were observed. It also contains unpublished data obtained from plates, kindly placed at our disposal, taken by Drs. Meggers and Foote in 1921, with total currents of the order of 1/2 ampere. These data are distinguished by asterisks in the column of voltages. It will be observed that in a few instances the voltage of appearance is smaller at high currents than at low. In some cases this is due to the weakness of the line in the low-current exposures, while in other it is to be attributed to successive excitation. In most instances the column of remarks shows which process is operative. No decision could be made for the lines 2834.08, and 4009.0 A.

At 10 volts, in addition to the completely developed arc spectrum, a few of the stronger lines of Cd^+ appear, namely, those classified in the report of Paschen and Götze, with exception of 2321.23 and3250.29

[2] Ann. d. Phys. 76, p. 145, 1925.

TABLE 1

Appearance Voltages and Classifications of Cadmium Lines

λ	Voltage	Current, Milli-amperes	Intensity	Remarks
2111.53	17	19	0	
2144.40	10	18	10	$5s-5p_1$ of Cd^+. Due to successive excitation.
	14	6	3	
2168.77	17	19	2	
2187.78	17	19	2	
	32	9	0	
2194.61	10	18	2	$5p_2-5d_2$ of Cd^+. Due to successive excitation.
	32	9	3	
2203.57	10	18	1	
	17	19	2	
2209.7	10	18	2	
	17	19	3	
2239.86	10	18	1	$2p_3-2p'_3$. $2p'_3=-2207.0$ cm^{-1}
2265.04	10	18	10	$5s-5p_2$ of Cd^+. Due to successive excitation.
	14	6	10	
2267.47	20*	800	0	$2p_2-2p'_2$
2306.61	10	18	2	$2p_3-2p'_2$ $2p'_2=-1457.7$ cm^{-1}
2312.87	10	18	2	$5p_1-5d_1$ of Cd^+. Due to successive excitation.
	23	6	2	
2325.7	17	19	3	Observed by Schenck.[3]
2329.27	10	18	0	$2p_1-2p'_2$.
2469.76	10	18	1	Enhanced at higher voltages. $2p_2-9D$
	16	20	1	
2487.96	20*	800	1	Probably due to Cd^+.
2494.25	10	18	1	$2p_2-8D$
	12	6-8	0	
2530.0	10	18	2	$2p_2-7D$
	12	6-8	2	
2540.08	25*	12-18	1	Recorded by Huppers, Zs. für wis. Phot. 13, p. 46, 1913.
2552.01	16	20	6	Recorded by von Salis.[2]
2558.03	17	19	–	$4p_1-4s$ of Zn^+. $4p_2-4s$ of Zn^+, at 2502.11, is hidden by a cadmium line.
2569.4	10*	800	–	$2p_1-8D$
2573.12	10	18	2	$5p_2-6s$ of Cd^+. Absent at 14v, 6 ma.
	22	11-12	2	
	23	6	3	
2586.86	10	18	2	$2p_2-6D$
	12	6-8	1	

TABLE 1 (*continued*)

λ	Voltage	Current, Milli-amperes	Intensity	Remarks
2607.2	10	18	2	$2p_1-7D$
	12	6-8	2	
2618.88	40*	700	1	Enhanced at higher voltages.
2621.15	10	18	1	$2p_2-5S$
2668.26	10	18	3	$2p_1-6D$
	12	6-8	3	
2672.68	20*	800	–	$5d_1-7f_1$
2674.74	17	19	–	Probably due to Cd^+.
2688.7	10	18	2	Classified by Takamine and Fukuda[5] as $2p_2-5p_2$.
	12	6-8	2	It is also $2p_2-5D$
2707.04	10	18	0	Enhanced at higher voltages.
	16	20	1	
2748.68	10	18	3	$5p_1-6s$ of Cd^+. Absent at 14v, 6ma.
	22	11-12	4	
	23	6	3	
2756.78	25	20	1	$2p_1-4f$.
2757.87	16	20	2	$2p_2-4S$.
2775.8	10	18	2	$2p_1-5D=2776.20$.
	12	6-8	2	$2p_1-5p_2$, at 2775.8, was observed by Takamine and Fukuda.[5]
2798.99	30*	300	–	$6p_1-11d_1$ of Cd^+.
2805.55	40*	700	1–	
2834.08	20*	800	1	Not enhanced.
	25	20	2	
	32	9	2	
2886.60	80*	400	4	$6p_2-11s$ of Cd^+.
2893.76	10*	400	0–	
2899.3	10	18	2	$2p_2-4D$.
	12	6-8	1	
2911.64	20*	800	0	$6p_1-10d_1$ of Cd^+.
	25	20	0	
	32	9	1	
2914.69	25	20	2	$5d_2-6f_2$ of Cd^+.
2927.90	30*	300	1	$5d_1-6f_2$ of Cd^+.
2929.29	20*	800	1	$5d_1-6f_1$ of Cd^+.
	32	9	0	
2943.89	40*	700	1–	$6p_1-11s$ of Cd^+.
2948.11	High	150-200	2	Enhanced at high voltages.
3001.2	9	3-6	1	$2p_2-4D$.
	12	6-8	5	
	14	6	2	
3030.67	20*	800	0	$6p_2-9d_2$ of Cd^+.
3092.34	20*	800	1	$6p_1-9d_1$ of Cd^+.
	44	9-11	0	
3141.61	20*	800	1	Perhaps $1S-2p_1$; calculated λ is 3141.16.

TABLE 1 (*continued*)

λ	Voltage	Current, Milli-amperes	Intensity	Remarks
3146.78	20*	800	1	$6p_1-10s$ of Cd^+.
3157.08	20*	800	0	Enhanced at higher voltages.
3224.21	10	18	–	
3250.3	16	20	–	May be $5p_2-4d_2$ of Cd^+. Absent at 14v, 6 ma.
	19	13	4	
	23	6	4	
3298.97	—	—	–	$2P-2p'_3$. Not observed on our plates
3343.15	25*		1	$6p_2-8d_2$ of Cd^+.
3385.35	20*	800	2	Not present at 23v, 6 ma. Steadily enhanced up to 80v, 400 ma.
	30	6	1	
3388.85	40*	700	2	$6s-7p_1$ of Cd^+.
3417.40	80*	400	1	$6p_1-8d_1$ of Cd^+.
3442.34	20*	800	1–	$6p_2-9s$ of Cd^+.
3483.04	20*	800	1	$5d_1-5f$ of Cd^+.
3495.35	25*	18-30	0	Not present at 23v, 6 ma. May be $5p_1-md_1$ of Cd^+.
	30	6	1	
3524.07	25*		1–	$6p_1-9s$ of Cd^+.
3535.82	12	6-8	1	May be $5p_1-4d_2$ of Cd^+. Due to successive excitation.
3665.5	30*	300	1	Recorded by Schenck.[3] Absent at 20v, 800 ma.
	40*	700	1	
3843.6	30*	300	0	Recorded by Eder and Valenta.
3902.7	20*	800	1	Recorded by Eder and Valenta.
4009.0	10*	800	1	Recorded by Schenck.[3] Absent at 23v, 6 ma.
	30	5.5	1	
4029.08	20*	800	0	$6p_2-7d_2$ of Cd^+.
	32	9	1	
4134.78	10*	800	0	$6p_1-7d_1$
	32	9	1	
4177.3	10*	400	1	Absent at 25v, 18-30 ma.
4511.34	10*	400	3	
4881.73	20*	800	2	Absent at 23v, 6 ma. and at 17v, 19ma.
	30	5.5	1	
5025.52	20*	800	2	
5337.73	20*	800	2	$5d_1-4f_1$ of Cd^+.
5378.42	20*	800	2	$5d_2-4f_2$ of Cd^+.

A. These are due to ionization of neutral cadmium followed by excitation of the ion, and all of them involve one of the three lowest energy levels of Cd^+, namely, $5s$, $5p_2$, and $5p_1$. Additional lines of Cd^+ should

appear when double ionization by successive impact occurs. We obtain 2552.22 A at 16 volts, 20 ma, while 2111.53, 2168.77, 2187.78, 2325.7 and 2674.74 A are seen at 17 volts, 19 ma. This voltage is in excellent agreement with the ionization potential of Cd^+, which is 16.8 volts, computed from the value of the 5*s* terms as given by von Salis.[2] However, it is not at all certain that these lines are due to Cd^+. None of them is classified, and only 2552.22 and 2674.74 are recorded by von Salis. In fact, at low currents the classified lines of Cd^+ do not appear in large numbers until the potential exceeds 25 volts. (Double ionization by single impact should be possible at 25.8 volts.) As one might expect, they are easily obtained at 20 volts or less when the current is large.

The 17-volt lines listed above may result from single ionization of the N_5 level of neutral cadmium. All we know concerning the N^5 level is that it must lie below 30 volts. (See National Research Council Bulletin on Critical Potentials, by Compton and Mohler, Fig. 16 on p. 110.)

Higher excitation stages are very poorly developed. No more lines are found at low current densities until we reach 25 volts. At first sight it is surprising that so few spark lines were obtained in the low-current exposures. However, it must be remembered that higher members of the subordinate series of Cd^+ lie at wave lengths below 2000 A.

We have obtained several new members of the series $2p-mS$ and $2p-mD$ of the neutral atom.

Of the previously unclassified lines which appear on our plates at 10 volts, we have classified all except 2209.7 and 3224.21 A. These classifications are listed in Table I.* Two lines which did not appear on our plates have also been classified. They are:

3011.7 A, $2p_1-4p_2$, observed by Schenck.[3]

3526.16 A, $2p_3-3p_2$, observed by Eder and Valenta.[4]

* It may be well to note the following impurity lines from the cadmium lists in volumes 5 and 6 of Kayser's Handbuch:

Ca, 4226.6

Cu, 3247.699, 3274.101.

Mg^+, 2795.616, 2802.771.

Pb, 2170.11, 2203.64, 2614.0, 2802.074, 2823.9?, 2833.174, 3089.23?, 3118.98?, 3682.6, 4057.7, 4245.8, 4272.9.

Zn^+, 2025.53, 2062.06, 2502.33, 2558.14.

[3] Astrophys. J. *14*, p. 116, 1901. In this paper the excitation stages are distinguished by studies of the length, breadth, etc., of lines in the spectrum of the spark after reflection from a rotating mirror.

[4] Kayser's Handbuch, Vol. 5, p. 278.

Takamine and Fukuda[5] have studied the spectra of metallic arcs in vacuo, in which the discharge was forced to pass through a constriction in a silica tube. For cadmium, in the region of greatest current density, they obtained the series $2p_1-mp_1$, $2p_2-mp_2$, $2p_3-mp_3$, and $2p-mf$. The lines $2p-mf$ which violate the azimuthal selection principle were stronger than the others; this is very interesting in view of the fact that our low-voltage, low-current arc fails to excite these lines.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
JANUARY 9, 1925.

Critical Potentials.—By K. T. Compton and F. L. Mohler Bulletin No. 48, 135 pp. National Research Council Washington, D. C. $1.60.

The last few years have seen tremendous activity in the study of the various phenomena arising from the effects of collisions between electrons and molecules, and of the interaction between radiation and molecules. The investigations of the minimum energy relations involved in such collisions have led to the determination of a series of important atomic and molecular constants, known under the now familiar names of Ionizing Potentials, Radiating Potentials, Resonance Potentials, etc. A closely related set of investigations has thrown a flood of light on the origin of spectra. The unifying and directing principle in all this field of physics, which has become increasingly apparent in recent years, is the conception of the atoms as a dynamical system, governed by quantum laws, and characterized by a set of energy levels. The greater part of the experimental work in this field may perhaps be regarded as the determination of these energy levels and the study of the transition of these energy levels and the study of the transition between them.

Under the concise and appropriate title of "Critical Potentials," Dr. K. T. Compton and Dr. F. L. Mohler have presented an extraordinarily thorough and comprehensive summary, up to May, 1924, of this subject, in which they themselves have been leading investigators. To those not working in this field, the Bulletin performs a real service in summarizing and in giving proper perspective to the work which has been done up to the present time. Those who are working on the subject will also appreciate it as an authoritative commentary and an invaluable reference book which will save many a hunt through the journals. Anyone planning to enter this field of physics will find no better way to save time than to consult the Report and to follow up, where necessary, the references given. Although no explicit statement of the problems yet to be solved is given, the attentive reader will have

[5] Japanese Jour. of Physics, *2*, Nos. 3-5, 1923.

no trouble in finding numerous ideas for investigation profusely scattered throughout the book.

Part I, by Professor K. T. Compton contains a very complete and concise description of the various experimental methods which have been employed in this field. Part II, by Dr. F. L. Mohler is a summary of the experimental results and their interpretation. No less than 180 papers are cited, most of them of recent date. It is a creditable achievement to have succeeded so well in digesting and correlating the somewhat bewildering mass of data now available.

Mention is made in passing of Townsend's studies of ionizing potentials and related topics by the indirect method of ionization by collision. In view of his adherence to this method, and his criticisms of what he calls the "valve" methods, that is, practically all the methods described in the Bulletin, a short discussion of his views would not have been out of place. It seems to the writer that the type of energy level diagram associated with the name of Grotrian would have had advantages over the type used in the Bulletin. It might have saved some confusion to those unfamiliar with spectroscopic notation, had an explicit statement been made as to the notation used. As most people who will use the Bulletin are probably more familiar with Fowler's Tables than with others, the authors might have considered using his notation. However these are minor matters. The Bulletin is a real and authoritative contribution to this rapidly growing subject and should prove of the greatest value to those interested in this field. It is written with unusual clearness and freedom from ambiguity.

This Bulletin is the first of a series to be published by a Committee the National Research Council on Ionizing Potentials and Related Subjects. Mention is made of other Reports on Thermal Ionization and on Properties of Excited Atoms to appear later. Should these Reports be as complete as the one here reviewed, the Committee will render service of the utmost value to those interested in this fascinating branch of physics.

A. LL. HUGHES

Expulsion of Electrons from light Atoms by Quanta of very high Frequency.—Although the probability of an electron being extracted from a given level of an atom by a quantum is greatest when the frequency of the quantum is barely sufficiently high to effect the extraction, and diminishes very rapidly as the frequency is raised beyond this point, yet it remains perceptible when the electron requires only a few kilovolts of energy to be extracted and the energy of the quantum corresponds to 600-1200 kilovolts; for gamma-rays of the stated energy extract the K electrons of elements as light as iron in perceptible number.—[J. Thibaud, Paris, C. R. *179*, pp. 815-818; 1924].

KARL K. DARROW

INSTRUMENT SECTION

RHEOSTATIC METHOD FOR REGISTERING OR MAGNIFYING DISPLACEMENTS AT A DISTANCE

By F. J. Schlink

The device to be described, on account of its simplicity, smallness of dimensions, and the fact that it can be constructed ready for use in a few hours time, has some advantages over other displaceometers of a more elaborate and precise character, such as Whiddington's ultra-micrometer, (modified and extended in application by Dowling, Thomas and others) and the McCollum and Peters carbon-pile telemeter. On the other hand, it has the disadvantage of registering in discrete steps rather than as a continuous function. It will afford sufficient precision in many practical problems, where a total displacement of 1 mm or more is available, which needs to be read to a precision of about .05 mm, and an accuracy of about .002 mm, and when a frictional retarding force of say 5 grams maximum can be tolerated.

An elementary form of successive contact displaceometer was described in 1922 (abstract in Physical Review, *19*, (3), p. 271; 1922) electrical contact being made on lines drawn with a carbon-base drawing ink. This method has certain obvious limitations as to the minuteness of spacing of lines obtainable along with durability, and particularly as to the lack of indication as to which of the several lines any given recorded contact represents, and on this account was limited in application to cases where the motion was of a simple character and began or ended in known relation to some fixed reference point, which made it rather unsuitable for irregular or oscillatory motions. For these reasons a method was developed which permits the individual contacts to be uniquely discriminated and to be quite exactly uniform in spacing without regard to any special skill in execution.

This consists primarily of a resistance wound of fine wire on a small cylindrical form, the successive turns being in actual mechanical contact, but electrically well insulated from each other. The insulation is removed in a strip perhaps 2 mm wide along an element of the cylinder, and along this path a contact spring or brush travels,

making contact successively with the turns of the coil. The technical difficulties encountered in constructing the first fine wire coils warrant description of the method in some detail.

Enameled IaIa wire, .003 inch (.08 mm) in diameter, the finest enameled resistance wire at the time available, was wound on a smooth and true brass tube about 12 mm in diameter, the tube being held in a lathe chuck and rotated steadily at moderate speed. If the tube is enameled or covered with paper to provide an insulating base for the winding, this will need to be done with particular care to avoid introducing even minute irregularities in the lay of the winding.

It is a simple matter to guide the wire so that the turns lie close against each other. To this end the cylinder should rotate smoothly and steadily, and the wire feed from its spool without jerks or irregularity. It is quite possible to prepare a length of 20 mm of winding without any other guidance than that given by the hand resting on a suitably placed smooth bar, but for the best work and for longer lengths, a lathe slide rest holding a wad of cotton or cloth through which the wire passes with some frictional drag, will be of great assistance. The beginning of the wire should be secured temporarily with sealing wax or deKhotinsky cement; the other end is similarly held when the winding is finished, care being taken to avoid the least slacking back of the wire before its end is secured. If the wire is fed steadily and without interruption and under approximately constant tension, a perfectly smooth and uniform helix will result, every turn of which, as may be seen under the microscope, is quite exactly uniform in spacing, and in mechanical contact with its neighbors.

The wire must now be held mechanically secure against displacment along or around the tube, which is accomplished by varnishing along the tube and over the winding in strips parallel to the axis, and also around the ends of the winding. It is of first importance to use a varnish which does not dissolve or soften the enamel insulation of the wire. Mogul varnish has been tried, though not entirely satisfactory on account of its brittleness when completely dried out. It does not, however, harm the insulation of the coil in any way. As the vehicle, petroleum naptha is recommended as least harmful in respect to the enamel insulation. Any varnish used should contain no solvents except petroleum, benzine or naptha; phenol products, coal tar derivatives and alcohol all have a deleterious effct on the enamel coating.[1]

[1] Electrical World, *80*, pp. 926, 927; Oct. 28, 1922.

When the varnish has dried sufficiently, the turns of the winding are bared for contact with the moving brush, by abrading gently along a narrow strip in the direction of the axis of the tube, with fine crocus cloth held on a narrow flat surface. Another element of the cylinder is bared, and on this, current leads are brought in by first applying minute drops of solder at each end, (using neutral zinc chloride flux); then tinned flexible copper wires are heated by means of a soldering copper applied a little way back from the end, and brought into contact with the solder drops, to which they will adhere without difficulty. The lead-in wires are then given mechanical support by cementing, or by binding to the cylinder with thread, to relieve the soldered joint from mechanical strain.

Before further work is done on the coil, it should be tested for insulation resistance, to make sure that no turns are in electrical contact with the tube. As for the brush, the design sketched in Fig. 1 was found very easy to make, and free from bouncing even at rates of motion equiva-

FIG. 1

lent to 5000 turns of the rheostat per second. (See Fig. 2). In fact the speed of contact travel seemed to have no limit within the capacity of the Duddell type oscillograph to record. The brush may have a thickness of about three times the wire diameter. The contact surface is flush with a cylindrical guiding surface of gum shellac or hard deKhotinsky, which is melted into a drop on the brush tip and then finished by file and fine abrasive paper into a smoothly curved guiding form as shown. Such a brush will operate without bounce and without opening circuit between turns (which is a matter of some importance to avoid useless motion of the oscillograph vibrator and hence error due to its lag) and will give a uniformly clear indication in the oscillogram, of the motion from turn to turn of the resistance coil.

In order to provide as nearly as may be, uniform increments of current through the oscillograph (when this or other short period instrument having as low a current sensitivity, is used as the registering instrument) for successive steps of brush motion, a circuit is used in which the coil is introduced as a potential divider, the two ends of the coil being connected to the voltage supply, and the oscillograph circuit fed through the moving brush. In order to reduce to the minimum, the

error due to change in potential drop per turn due to the variation in current flow through the coil occasioned by the changing amount of the branch current through the tap circuit of the brush, a current of a full ampere was passed through the coil, cooling being applied to the tube by a gentle air blast, and the brush, acting as potential tap, drew off from 0 to .035 amperes according to its position, the .035 ampere maximum corresponding to full deflection of the oscillograph element used. This increment of current, through the oscillograph branch, occasioned a distortion in the displacement scale of the record that was negligible for the purpose in hand, so that replotting of the oscillogram (which is always possible when distortion of scale is a factor, or a larger diagram is needed for differentiating, for example), was not necessary. In the use of the method with indicating galvanometers, the current sensitivity will usually be so good as to make the scale distortion negligible; when this is not the case, the coil may be wound on a cone of slight taper to provide the desired compensation.

When necessary the safe current flow through the coil can probably be multiplied by a considerable factor, by the use of cooling water flowing through the tube and an air blast on the outside. Moreover, in some cases, advantage may be taken of the heat capacity of the form on which the wire is wound, since oftentimes the heavy current need flow for only a small fraction of a second in order to obtain the desired record. In this case a solid cylinder of copper or brass could be used. When the current through the coil is such that it will attain a rather high temperature during the course of a registration, precautions should be taken to prevent heating of the brush tip to such extent as will melt the cement forming the guiding shoe, or if necessary for the device to work steadily under high temperature conditions, the guiding shoe may be made of a more durable and heat resistant insulator than in the construction described.

The winding pitch is found to be identical with the diameter of the wire, within the errors of measurement. Measurement of this pitch by means of a filar micrometer presents some difficulty on account of reflections from the glossy curved dark surface of the enamel, but such detailed measurement is hardly likely to be needed, as examination under low power microscope (10 to 20x) will serve to determine beyond question whether successive turns of the winding are in contact along the element used for making contact with the brush.

In Fig. 2a is shown a specimen oscillogram using a displaceometer coil having turns of No. 38 enameled copper wire (diameter over in-

sulation .0047 inch, .12 mm). Each step of current corresponds to motion of .12 mm at the brush and is hence magnified about 18 times in the original oscillogram. It will be noted that every step of movement is plainly recorded. Fig. 2b shows the records of very irregular and rapidly accelerated motions having a period of about .015 sec., the displacement being recorded in 14 equal steps of .0035 inch (.09 mm). In the original oscillogram, all of the steps are distinguishable, except in regions of extreme acceleration as at *c*.

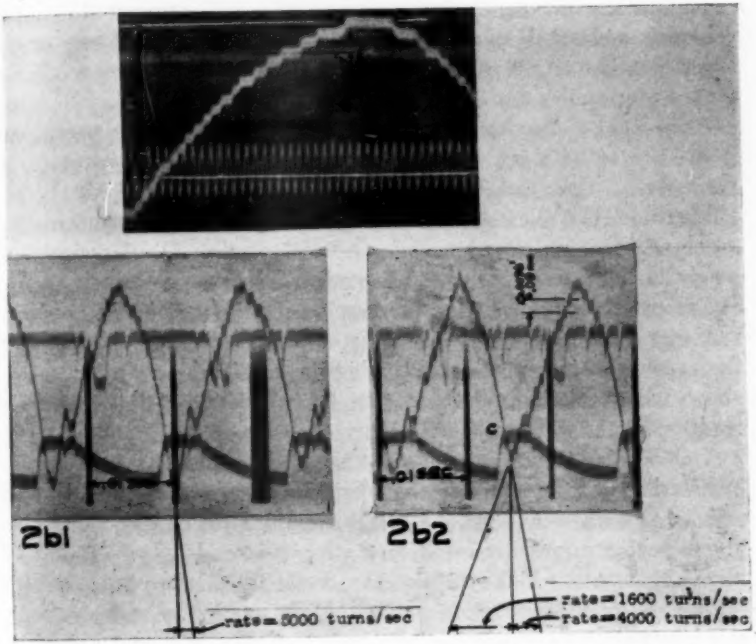

FIG. 2. *a—step-by-step displacement record at low speed (maximum 1000 turns/sec.)*
b—step-by-step displacement oscillogram of rapid oscillatory motion involving large accelerations.

The arrangement described is quite durable in service. The slightest touch of vaseline to the working surface of the coil will reduce wear to a minimum. If the apparatus is in constant use, some care in selection of wire and brush material will enhance the life considerably. A phosphor bronze brush carrying a small lead content should give good service on IaIa wire.

The ordinary use of the device will be for reproducing linear or angular deflections at a distance, as for example the amount of opening

of a valve. In such applications, using a pivot galvanometer as the registering means, the device serves as an inexpensive substitute for the induction balance, e.g., in connection with pressure and temperature indicating and recording instruments.[2]

By a combination of two displaceometer elements, one actuated by piston displacement and one by the deflection of a piston loaded with a much stiffer spring than that used in the ordinary engine indicator, a remote recording engine indicator (pressure—volume relation) capable of registering correctly at high engine speeds, can be prepared without difficulty, and, when an oscillograph is already available, at very much lower cost than any of the quite elaborate optical devices now available for the purpose.

On account of the cheapness of the device and the ease of reproducing it in case of accident or defect, several other applications suggest themselves. One such, developed under the direction of Mr. F. H. Hibbard of the Western Electric Company, is an instrument for accurately reading time intervals on oscillograms. Displacements of a hair line on a traveling slide adjusted to coincidence with the events of the record, are shown greatly magnified in the readings of a microammeter connected in a potential tap as described above, thus sparing the eyes of the computer and eliminating to a large extent errors of observation common in the use of the finely graduated scale otherwise required for the measurement.

A device for testing springs or other elements having high elastic hysteresis, such as specimens of fabric or rubber, the cyclic test of which has always involved difficulties in apparatus design, can easily be made by an electro-mechanical combination of two displaceometric rheostats, which will plot automatically the stress-strain loop for a cycle of loading and unloading, or any number of such cycles in rapid succession (a determination which is coming to be recognized as of much importance in materials testing work.) One displaceometric rheostat would connect to and control the deflection of a pivot galvan-

[2] For references to such applications, see Georg Keinath, Neuerungen in Bau elektrischer Messgeräte E. T. Z., Heft *33*, pp. 905-910; 1921. E. A. Griffiths, Electrical Instrument Equipment for Aircraft, Beama, *10*, pp. 299-307; Apr. 4, 1922. For papers on registration of motions at a distance, the following references and the Bibliography for Measuring Instruments, J. Opt. Soc., *9*, (3), pp. 309-321; 1924. Messen von Schwingungen und Drehmomenten mittels des Oszillographen, R. Elsässer, Z. v. d. I., *68*, (20), May 17, 1924.

Notes on Electrical Measurement at a distance, Neumann, Zeitschrift f. Fernmeldetechnik, Mar. 5, 1920.

Use of an Oscillograph in Mechanical Measurements, H. L. Curtis, paper to be presented at Midwinter Meeting of A.I.E.E., New York, Feb. 9-12, 1925.

ometer carrying on its pointer system a piece of photographic film thus rotated through an arc (or by a possible modification given a translation) proportional to the strain of the specimen. The other rheostat actuated by the deflection of the spring or pendulum which measures the force applied to the specimen, would modulate a current deflecting an oscillograph vibrator or ordinary reflecting galvanometer mirror by which the stress component is projected as a spot of light moving normally to the direction of motion of the film on the galvanometer pointer. If necessary to record rapid motions without introducing errors due to slowness of period of the galvanometer, and imperfect damping, it may be desirable to resort to the micro-diagram method, using a stiffer restoring spring, and correspondingly small pointer deflection, examining the resulting record with a microscope or optical projector, A better scheme in such cases may be to utilize the familiar device of a stationary film and two mirror galvanometers having their axes at right angles, the first mirror reflecting its beam onto the second, so that the motion of the image of the light source represents the resultant of the motions of the two galvanometer mirrors.

When a considerable length of travel is available for the brush, or low current sensitivity is required, copper wire, which is cheaper and more easily obtainable in small sizes, enameled, than wire having a low temperature coefficient such as IaIa, may be used. In such cases temperature errors should be guarded against by small or momentary currents and adequate cooling of the coil. Of course in cases where a record of the instant of traverse of the brush over the several turns of the coil is all that is required, without regard to absence of distortion in the plot, such errors are of small consequence. In such cases also, a simple series circuit from battery, through the coil to the oscillograph, may be used. While this arrangement will not serve at all well where many steps of motion are to be recorded, it has the advantage in other cases that no cooling problem is involved, or any need for a steady source of moderately high potential.

AMERICAN ENGINEERING STANDARDS COMMITTEE,
29 W. 39th ST., NEW YORK, N. Y.,
DECEMBER 20, 1924.

The Structure of Crystals.—By Ralph W. G. Wyckoff, Physical Chemist of the Geophysical Laboratory of the Carnegie Institution: 462 pages: Book Department of the Chemical Catalog Company, Inc. New York, $6.00 net.

This book contains a description of the analysis of crystals by a combination of the theories of point and space groups and of the ex-

perimentally determined directions and intensities of x-rays reflected by the crystals.

The first chapter describes briefly the way in which points equivalent to a given point are distributed in space about a center, line or plane to conform with the various symmetry conditions of the crystal, (the theory of point groups). It also discusses the way in which such point groups may be distributed through space in a space lattice also to conform with the conditions of symmetry, (the theory of space groups). It is assumed that the atoms in a crystal (or at least those which have a predominating influence on the crystal's properties) occupy the positions determined by the above theories.

The following four chapters contain a brief outline of (a) some of the fundamental characteristics of x-radiation; (b) the reflection of x-rays by crystals and the intensities of the reflected rays; (c) the production and interpretation of Laue photographs; and (d) the instruments and methods employed in analyzing x-ray spectra, including chiefly the Laue photographs from single crystals and photographs obtained from powdered crystals. It is assumed that the directions and intensities of the x-rays diffracted by a crystal are correctly given by the theory that such diffraction results from the interference of secondary x-rays coming from the various atoms, or ions in the crystal in amounts proportional to the numbers of electrons in them.

Chapter seven is devoted to a description of the way in which the theory of space groups should be combined with the results of analyzing x-ray spectra in order to deduce the positions of the atoms in crystals.

Chapter nine to thirteen inclusive contain a somewhat detailed statement of the results obtained in analyzing all the crystals that had been examined up to January 1, 1924. These results have been critically examined by the author of the book and the fact that a man who has devoted much time and thought to the subject gives his opinion as to the weight that can be attached to the results of experiments, adds greatly to the importance of this section.

The last two chapters contain descriptions of incomplete crystalline and non-crystalline diffraction phenomena and some applications of diffraction information in such questions as the existence of molecules, the nature of valence, atomic radii, magnetic phenomena, etc.

The book concludes with a fairly complete bibliography of crystal structure data and some useful tables.

The book has been well written, and, except that some of the pages contain crooked lines of words and some of the 213 carefully drawn figures have been so reduced that the smallest letters are almost illegible, it has been well printed.

The fact that its author has carried through so much original and important research in the field covered by the book makes it well worth careful study by everyone interested in either x-rays or crystal structure.

WILLIAM DUANE

ELECTROSTATIC VOLTAGE MULTIPLIERS

By Alfred W. Simon

In a previous paper[1] the author has described a simple device, which serves to step up the voltage of a battery, or any other constant source, to a large multiple of its original value. The machine described is but one example of a whole family of such machines, which we shall designate by the term electrostatic voltage multipliers, and with which we are concerned in the present work.

A practical defect of the simple machine already referred to is that it delivers current in pulses at the rate of one per revolution, so that due to leakage, which usually occurs in practice, the potential of the load is not constant but exhibits a definite ripple. A method of reducing this ripple is to use instead of a single carrier, as was actually used in the device mentioned, a large number of carriers, in order to make the

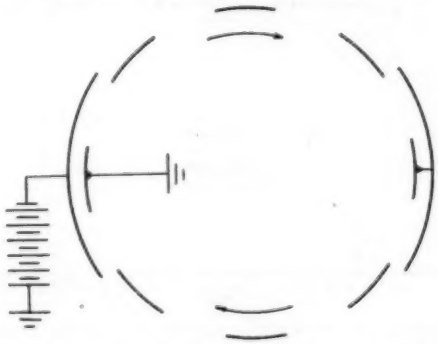

Fig. 1. *Non-symmetrical, direct multiplier. An influence multiplier is derived from this machine by merely breaking the battery connection, leaving the inductor charged.*

pulses more frequent and the ripple, consequently, of smaller amplitude. We are thus led to the construction of a machine of the type represented diagrammatically in Fig. 1. In order to produce a high transformation ratio, a third element, called the receiver, has been added. The function of the receiver is to withdraw as much charge as possible from the carrier, for this purpose it is so shaped as to nearly completely enclose the carrier. Since the carriers are charged directly from the battery, this machine may be termed a *direct*, electrostatic voltage

[1] This journal *9*, p. 345; 1924.

multiplier, to distinguish it from the *influence* multiplier, in which the carriers are charged by induction, and which may be derived from it by merely breaking the battery connection, leaving the inductor charged. A machine of the influence type would function equally as well as one of the direct type were it not for leakage, which gradually depletes the charge of the inductor. However, the latter difficulty is avoided in a *symmetrical, influence* multiplier, which is derived from a *symmetrical, direct* multiplier (Fig. 2) by breaking the ground connections. While there is little constructional difference between the two types, the symmetrical influence machines have the great advantage

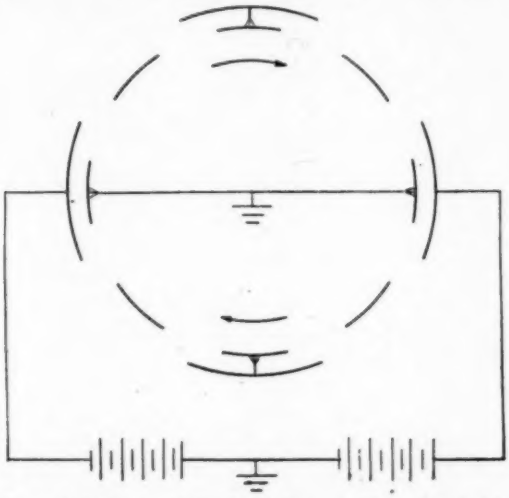

FIG. 2. *Symmetrical, direct multiplier. An influence multiplier is derived from this machine by simply breaking the two ground connections.*

that they can be operated in series, the transformation ratio of machines connected in series being the product of the transformation ratios of the separate machines. For example, three machines each with a transformation ratio of 10 may be connected in series (or combined into a single machine) to give a transformation ratio of 1000. The successive machines or stages must, of course, be constructed for increasingly greater operating voltages; and in practice leakage and breakdown will set a limit to the highest potential attainable; nevertheless, theoretically, one can in this way attain any constant multiple of a given potential. This fact is not astonishing in the field of electrostatics, for it can be shown that theoretically an ordinary static machine

steps up *indefinitely* any small difference of potential imparted to its inductors.[2]

The similarity of these machines to the ordinary influence static machines, as well as their points of difference, are well illustrated by Figs. 2 and 3. An ordinary static machine is derived from the machine of Fig. 2 by simply breaking ground and battery connections and, further, connecting inductors and receivers together in pairs as shown in Fig. 3. Under these conditions the machine becomes an ordinary influence machine of the Voss or Toepler-Holtz type. A careful study of Figs. 2 and 3 also shows how ordinary influence static machines of the Voss, or even of the Wimshurst type, may be converted into constant potential static machines or, as we have termed them, electrostatic voltage multipliers. As a general principle it may be stated in this connection that *separately excited* static machines are inherently *constant potential* machines.

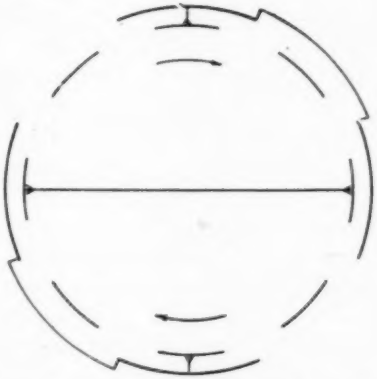

FIG. 3. *An ordinary static machine. It is derived from the multiplier of Fig. 2 by breaking both ground and battery connections, and connecting receivers and inductors in pairs as shown.*

So far our discussion has centered on machines with a definite number of carriers. Such machines are discontinuous current machines, although, as the number of sectors is indefinitely increased, they will approximate continuous current machines. While it is obviously impossible to use an infinite number of sectors, the same result can be accomplished in another way: namely, by using no sectors at all. For it is well known that a sectorless static machine behaves like one with

[2] A. W. Simon, Phys. Rev. *24*, p. 690; 1924.

an infinite number of sectors and gives continuous current.[3] The same principle applies to an electrostatic voltage multiplier. Sectorless machines have possibilities for high voltages, but a more detailed consideration of these machines must be left to a later paper. We shall merely emphasize here that they do afford a means of getting continuous current.

Historically the first, and also one of the simplest, electrostatic voltage multipliers, is the electrophorous. From the theoretical point of view it is the prototype of the *influence* multipliers; whereas the simple condenser device mentioned at the beginning of this article is the prototype of the *direct* multipliers.

Next in historical order, we may include the whole family of frictional static machines. These are essentially electrostatic voltage multipliers of the sectorless type. In the light of our present theory we are led to conclude that frictional static machines are essentially constant potential machines. The initial source in this case is very likely the contact emf of the rubbing substances. Of the later types of electrostatic voltage multipliers must be mentioned the machine of Planté,[4] which is simply a device for charging condensers in parallel and then connecting them in series.

However, the first example of the type of electrostatic voltage multiplier with which we are primarily concerned in the present work is a machine invented by Lord Kelvin,[5] and used in connection with the Atlantic cable. Lord Kelvin's machine was a non-symmetrical machine of the influence type. It is not to be confused with his replenisher, which was an ordinary static machine and was used as an "adjunct" to charge the inductor of the multiplier. Lord Kelvin kept the inductor of the multiplier at constant potential by means of the replenisher and a gauge electroscope, and recognized that under these conditions the output voltage was constant.[6] If we replace the replenisher by a battery, or other source of constant potential, we convert Lord Kelvin's machine into one of the type of Fig. 1. An interesting point in this connection is that the machine of Fig. 3 is essentially the replenisher of Lord Kelvin.

From their similarity to ordinary static machines, the qualitative theory of the electrostatic voltage multipliers is easily given. If, for

[3] V. E. Johnson "Modern High Speed Influence Machines" p. 102; London, 1922.
[4] G. Planté, C. R., *85*, p. 794; 1877.
[5] Sir W. Thomson "A Reprint of Papers on Electricity and Magnetism," p. 334; 1894.
[6] Sir W. Thomson, loc. cit.[5]

example, we consider the machine of Fig. 1 we find that when the carrier is earthed it becomes charged with electricity of sign opposite to that of the inductor. It then breaks contact with the ground and moves out of the positive field of the inductor. Hence its potential must decrease. As it continues to rotate it comes in contact with the receiver brush and gives up part of its charge to the receiver, lowering the latter to a *negative* potential. The difference of potential between inductor and receiver therefore becomes greater than the emf of the battery (the negative pole of the battery being at zero potential). Each carrier augments the negative charge of the receiver. However, this process cannot go on indefinitely, for if it did, the potential of the receiver would eventually become low enough to neutralize the effect of the positively charged inductor in inducing charge on the carrier, and no further charge would be carried forward. Actually the process will, of course, stop somewhat short of this stage.

Our qualitative theory leads to the result, therefore, that the potential of the receiver must decrease until it reaches a definite constant value, which will depend on the geometry of the machine and further be proportional to the emf. applied.

A machine of the symmetrical influence type as shown in Fig. 2 was actually constructed in this laboratory. The carriers were 8 tinfoil sectors, each of an angular width of $22\frac{1}{2}°$, mounted on an ebonite disc 8 inches in diameter. The disc was rotated by means of a motor. The inductors and receivers were of the same general shape as the quadrants of an electrometer, except that they were "octants," subtending an angle of 45°. The carriers covered both sides of the disc. One pair of oppositely situated octants formed the inductors, the other pair, the receivers. An insulated cross arm (polarizer) with brushes at its extremities was placed so as to connect together a pair of opposite carriers when they were in the center of the inductors. Simultaneously, another pair of brushes connected the pair of carriers within the receivers to the latter. The two inductors were connected to opposite poles of a battery, and the receivers to the load. This was usually a Leyden jar with a Braun electrostatic voltmeter in parallel.

When the machine was worked, it was found that the voltage across the load rose rapidly to a constant value, which was independent of the capacity of the load and was a definite multiple of the exciting emf. This multiple, which is the transformation ratio of the machine, was observed to be about 12. While the final voltage was independent of the capacity of the load, the rapidity with which the potential rose to

its final value depended on the load, decreasing with increasing capacity. The potentials attained were of the order of magnitude of 2000 volts. This particular design, of course, was not intended for high potentials: it was designed primarily to test the above theory.

The results attained with the device were, however, so satisfactory that machines of the type discussed in the present paper may be recommended as substitutes for high voltage batteries in all those experiments where a high potential but little current is required. Indeed, it may be possible to construct large machines on the same principle to give considerable current and actually replace high potential batteries in many laboratory experiments. At any rate, small machines of this type should prove useful for chargimg electroscopes, ionization chambers, etc. It should be possible to construct small models with discs only a few inches in diameter and excited by flashlight batteries for charging electroscopes. Finally, machines of the sectorless type on a large scale may be constructed to step up high D. C. voltages, attained from a kenotron-transformer system, say from 30,000 to 100,000 volts or even higher. Experiments along this line are now in progress in this laboratory and will be reported in a later paper.

In conclusion, I wish to thank Professor A. H. Compton for the encouragement he has given me in this work, and also Mr. R. D. Bennett for the assistance he has given me in the construction of the machines.

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Absorption by Sodium Vapor.—The problem is to determine the absorption for frequencies higher than the series-limit, quanta of these frequencies being such as would eject the valence-electron completely from the atom and with kinetic energy to spare, as electrons are ejected from the inner levels of atoms by quanta having more energy than just the amount sufficient to extract them. The data obtained by a photometric method previously described in this Journal, *8* p. 471, 1924, show that the absorption of light by sodium vapor has a sharp maximum pretty accurately located at the limit of the principal series at 2414A; going from this point towards higher frequencies, the absorption decreases steadily to the limit of observation at 2150A; going from it towards lower frequencies, the absorption decreases to a minimum near 2450 and then increases again. (In the latter case the absorption is measured between the lines of the principal series.) Owing to the possibility of absorption-bands in this region the author hesitates to draw definite conclusions regarding the problem stated above. [G.R. Harrison, Stanford and Harvard; Phys. Rev. *24*, pp. 466-477; 1924.]

KARL K. DARROW

A DEVICE FOR DEMONSTRATING SHORT ELECTROMAGNETIC WAVES

By R. M. Fisher

The universal popularity of radio broadcasting calls attention to the need for some simple way of demonstrating the fundamental properties of electric waves. The apparatus described below has much to recommend it for use in popular and elementary lectures on the subject. It is easily built, and the extreme simplicity of its electrical connections, made possible by using a crystal detector, is of great pedagogical advantage. Also the shortness of the waves employed enables the lecturer to show such phenomena as standing waves in a room of ordinary size.

A similar arrangement has been used for research[1] and in a course of experimental lectures given at the Cornell laboratory by Professor Ernest Merritt. Unfortunately, it has often proven exceedingly unreliable when in actual use before an audience, all manner of disturbances masking the effects desired. Recently Professor Merrit suggested to the writer the task of studying, and eliminating so far as possible, the causes of this erratic behavior, and the arrangement described is one that was finally found satisfactory. Particular attention is called to the form of the receiving circuit; it was in this that the chief improvement was made.

THE SOURCE OF WAVES

The sender (Fig. 1) has as its antenna two metal arms, each ending in a blunt conical spark gap electrode of brass. Sparking is produced by connecting the secondary of an ordinary Ford ignition coil unit to the gap. Water resistances, (glass tubes filled with distilled water) serve to damp out oscillations in the secondary circuit. The sparks pass in oil, either kerosene or parafin oil, the latter having the advantage of being non-inflammable.

The emitted wave-length depends on the total length of the antenna; an antenna 20 cm long gave waves about 45 cm in length. For reasons discussed later, it is preferable to use somewhat longer waves, one meter being perhaps the optimum wave-length for all purposes.

[1] "The Silicon Detector used with Short Electric Waves, and Theory of Contact Rectifiers" E. Merritt. Abstract of a paper presented at the Washington meeting of the Physical Society, April 21, 1911. Physical Review, *32*, p. 630, 1911.

"A Study of the Law of Response of the Silicon Detector." L. S. McDowell and F. G. Wick, Physical Review, *8*, p. 133; 1916.

The sparks must, of course, be oscillatory, and best results are obtained when the electrodes of the spark gap are very close together. Successive sparks should be of equal intensity; this means careful adjustment of the movable contact, or buzzer of the spark coil so that the sound of it is of uniform pitch. The sparking causes the formation of bubbles, due to the breaking down of the oil in the gap. No suitable liquid could be found which would not decompose in a spark gap, and those already mentioned were found as satisfactory as any that were tested. Variations in intensity caused by bubble formation can be reduced to a minimum by keeping the electrodes barely covered with oil.

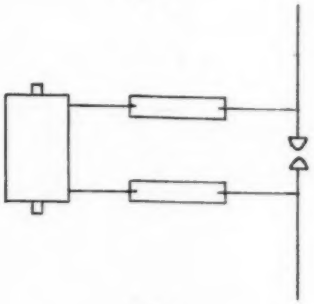

FIG. 1

THE RECEIVER

The receiving antenna, either a straight brass rod, or a loop of brass wire, is coupled to a secondary circuit simply by being placed close to one side of it. The secondary is a small rectangular loop of wire having in the middle of one side a crystal detector, and on the other side, symmetrically placed, a telephone condenser of large capacity in series.

This circuit is untuned; oscillations induced in it are partially rectified, and become a series of direct current impulses, capable of producing a deflection of the galvanometer which is connected to the terminals of the condenser. The purpose of this condenser is analogous to that of the air chamber of a force pump; it serves to steady the galvanometer current between pulses. A spot of light, reflected from the galvanometer mirror, indicates by its position on a wall scale, the magnitude of the secondary current.

The symmetry of the secondary loop seems to be essential to favorable operation, but the position and length of the twisted wires leading

to the galvanometer do not apparently matter. The antenna and secondary are therefor mounted on a movable stand, and the galvanometer wires made long and flexible, so that the stand can be placed wherever desired.

The following are details of the receiver in use.

Detector—Erla Fixed Crystal Detector.
Condenser—Telephone, capacity 1 microfarad.
Loop Dimensions—Length 7 inches, width 1 ½ inches.
Linear Antenna—of brass tubing, telescoping, adjustable from 1 ½ to 2 ft.
Loop Antenna—Rectangular, length 8 in., width adjustable from 0 to 8 in.
Galvanometer—D'Arsonval, sensibility 1500 megohms, reflects a spot of light on a scale 3 meters distant.

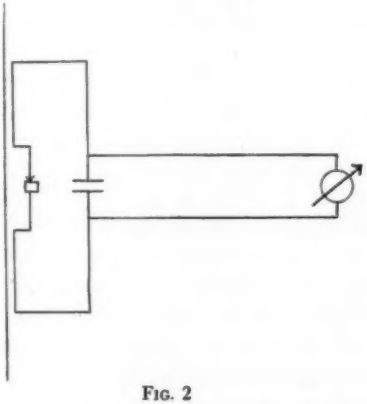

FIG. 2

The detector circuit, containing a rectifier, should be incapable of tuned oscillations, but actually the rectification is only partial, and the secondary responds somewhat when the antenna is not in place, the effect increasing when shorter waves are used. As this is not desirable, it may be greatly reduced by making the secondary loop small, and enclosing it in a metal box with open sides through which the antenna projects.

In addition to the apparatus described, the demonstration requires a parallel wire screen, which is made by fastening copper wires parallel to each other, and two inches apart, to a wooden frame six feet square. In the discussion of phenomena which can be shown, this will be referred to as 'the frame.'

PHENOMENA DEMONSTRATED

The following are some of the effects which this apparatus has been used to show.

1. *Tuning*—by adjusting the length of the linear antenna, or the area of the loop antenna.
2. *The opacity* of conductors, and wire screens.
3. *Interference* and standing waves.

When the wire frame is held behind the receiver, waves that reach it are reflected, and interfere with the oncoming train. By moving the receiver toward or away from the screen, its position may be made alternately a node or a loop. By marking these positions, the wave length can be measured. The same effect can be obtained if the receiver is left stationary, and the screen moved behind the sender.

4. *Reflection.*—The receiver may be screened from waves coming directly from the sender, and made to respond to waves reflected from the frame held off at one side.

5. *Polarization, and nicol prism analogy.*—The waves from the sender are plane polarized, and will not affect a linear receiving antenna when it is placed at an angle of 90° to the sender. When the receiver is so placed, if then the wire frame is placed between, and its wires turned to an angle of 45° with the sender, the receiver responds, "the light is restored between crossed nicols."

When sender and receiver are parallel, the frame placed between them, its wires at right angle to both, allows the waves to pass unhindered. If the frame is now rotated in its own plane the response of the receiver, indicated by the galvanometer deflection is gradually cut down, and becomes zero when the frame has turned 90°; extinction of light by a nicol prism.

6. *Direction of the state and magnetic components of the waves.*—The loop antenna has a gap in one side. When the antenna is in a position so that this side is parallel to the sending spark gap, it will respond to the electrostatic field of the oncoming waves. When the loop lies in the same plane as the sending antenna, it is in a position to be cut by the magnetic lines of force of the wave, since these are perpendicular to that plane. Hence the loop may be placed so that it is affected by the static component alone, by the magnetic component alone, or by both at once. It may be shown approximately that the response to the electrostatic effect is of the same magnitude as that to the magnetic effect, and that both together give twice the response of either alone.

Using the frame to set up standing waves, as described, and with the loop alternately in the static and magnetic positions it can be shown that static nodes coincide with magnetic maxima and vice versa.

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MECHANICAL THERMOSTATS*

By J. R. Roebuck

General Considerations.
A. Baths.
1. Form, Table of Fluids.
2. Stirrers.
3. Insulation.
B. Heaters and Coolers.
1. Gas flame.
2. Steam and hot water.
3. Electric heating.
4. Cold tap water and ice.
5. Expanding compressed gas.
C. Responding Devices.
1. Bi-metallic strip.
2. Volume expansion type.
3. Electrical resistance.
4. Thermocouples.

General Considerations

Mechanical thermostats are all devices for controlling the heat supply of a system in such a way as to maintain its temperature constant. Beside the bath there is required a device for responding to a difference of temperature and devices for supplying and controlling a heat flow. The devices of the various classes, A, B, and C in the table above, may be combined in a variety of ways. The particular choice is determined by the availability of the required means and by the suitability for the desired purpose. The wide variety of uses of such devices and the broad latitude in their design render specific descriptions of little help in most cases, so that in what follows general considerations will be discussed leaving the detailed application to the reader.

Baths

Form: Table of Fluids. The shape and size of bath must be determined by its intended contents and liberal allowance should be made for circulation of the bath fluid. Galvanized iron, zinc, copper, are suitable materials. Compact shape is desirable both for thermal protection and for effective stirring.

* One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of Physical measurements. See Editorial in this Journal *9*, p. 410, 1924.

In the following table are possible bath fluids with their approximate effective temperature range.

Substance	Range
1. Fused inorganic salts	200–1600°C
2. Lead-tin alloy	200–600
3. High temperature lubricating oil	100–300
4. Tempering oil	50–300
5. Glycerine	100–270
6. Commercial vegetable fats (Crisco)	100–300
7. Light lubricating oil	30–200
8. Water	0–80
9. Brines	− 40–+120
10. Kerosene	− 40–+ 75
11. Gasoline	
12. Casinghead gasoline and Petroleum ether	−130– 0
13. Acetone	− 94–+ 56
14. Ethyl alcohol	−114–+ 78
15. Toluol	− 95–+110
16. Isopentane	−160–+ 28
17. Propane	−190–− 45
18. Propylene	−190–− 48

Notes: No. 1, Fused salts (Straube, Electrotechn. Z., *29*, p. 755; 1908). No. 2, See (White, Phys. Rev., *31*, p. 682; 1910). Nos. 3 to 6, The upper limit for such organic compounds is set by decomposition, smoke and spontaneous ignition. They may be carried higher under pressure. No. 3 is perhaps the most available; this includes the best high temperature gas engine oils and most of the purified mineral oil (Russian mineral oil) sold for medicinal purposes. No. 5 has a very irritating smoke. No. 6 is solid at ordinary temperatures and must be melted but becomes liquid at ordinary temperature after continued use at high temperatures. No. 9, most of the brines are very corrosive of metal containers. No. 11 and 12 are hard to set limits for on account of uncertainty in composition, and they become much more viscous at lower temperatures. No. 14 becomes very viscous before freezing. No. 17 must be kept cold or stored under pressure. No. 18 (Ber., *53*, p. 751; 1920). Air or other gas gives the greatest range of temperature but is a very poor bath fluid except at very low temperatures on account of its very small volume heat capacity.

Stirrers. The available stirrers are

(1) Air from small jets disposed about the bath, especially effective for tall baths, but objectionable often on account of both heat and evaporation losses.

(2) Screw propellers mix the liquid well especially if several can be used on the same or different shafts and power is not spared. They are best when almost in the open and are not very effective in driving a liquid rapidly over a more or less predetermined path.

(3) Centrifugal propellers are more effective in this latter case, as a wide range of velocities are under command and the liquid may be readily driven to outlying parts.

(4) Reciprocating parts are ineffective as general mixers unless relatively large.

Insulation of Bath. Available materials, wood, sawdust, cork powder, cotton, paper, felt, asbestos, steam pipe covering, brick, infusorial or diatomaceous earth. Very perfect insulation is profitable by reducing the magnitude and abruptness of external disturbances and by minimizing the load on the heater. The lag, however, retards the setting up of steady conditions.

HEATERS AND COOLERS

When the working temperature is at least one or two degrees above (or below) the extreme upper (or lower) limit of the room temperature variation, then a controlled heater (or cooler) is sufficient to keep the temperature constant. But when the working temperature lies within the limits of the temperature of the room, it becomes necessary (a) to arrange to use a heater or cooler as is required, which is hardly feasible if the alternation is frequent, or (b) to use a continuous heating and cooling, making one steady and controlling the other (heater usually).

Gas flame. Gas flames as heaters have the advantage of low operating cost but the disadvantages are serious: (a) A burner which will not cover the apparatus with soot, will not strike back, and yet burn over a wide range of gas flows is very difficult to obtain. (b) All gas supplies vary in pressure and this generally results in variation in the temperature of setting of the control mechanism. (c) The heat input is limited to an area on the bottom of the bath which is not protected by insulation and the heat must be distributed through the bath by very effective stirring. (d) The fire hazard of an open flame may be reduced by using only metal tubing but is objectionable.

Steam and Hot Water. When available low pressure steam or hot water is readily used by employing an electrical contact to operate a valve which may either control the primary flow or simply divert all or part of a steady flow.

Electric Heating. When available, electrical heating is much to be preferred. The heat may be delivered approximately where the loss occurs and the controls may be made very simple and positive. As heating elements one may use: (a) Incandescent lamps with the socket set in the wall of the bath and a thin rubber tube drawn over the socket and base of the bulb. (b) Coils of bare or covered wire disposed about the bath. With water as bath liquid electrolysis quickly ruins such exposed coils even with alternating current. (c) Very compact and flexible enclosed heaters may be bought. (d) The bath liquid may be made conducting and heated by a current between resistant electrodes. All exposed metal parts are rapidly attacked and the heating is usually badly distributed. (e) The heater wire may be disposed about the bath, as flat coils or wound around the bath with paper, cotton, asbestos or mica insulation, depending on the temperature and the energy input.

Cold Tap Water and Ice. Since the tap water supply is usually a few degrees below room temperature, it is the most convenient means for cooling a bath slightly while at the same time holding it near room temperature by a controlled heater. Where the desired temperature is below room temperature, such a water flow may be controlled by the same mechanism as with steam or hot water, so giving the desired temperature control.

For obtaining temperatures down to the freezing point, commercial ice is the best means. The bath may be surrounded more or less completely, depending on the desired temperature, by another bath of ice and water, and the regulation obtained by a controlled heater. By adjusting the area exposed to the ice-water the necessary heat may be minimized.

Expanding Compressed Gas. For temperatures below the freezing point, there is required some type of refrigerating plant—air, carbon dioxide, ammonia, sulphur dioxide—where the gas is allowed to expand or to evaporate. This is discussed in another article in this series.

RESPONDING DEVICES

Bi-metallic Strip. 1. Suitable bi-metallic strip, e.g., invar-nichrome (chromel), may be bought (Chem. Abs., 16, 3560, 1922). To be sensitive the strip must be long and thin and is best coiled flat. The supporting end may be adjustable for rough setting while the fine setting is made by shifting the external contact at the other end. For rough control (about $\pm 1°C$) a straight strip will answer. Here the

force involved is large so that sticking and failure to make contact do not give trouble. But as the sensitiveness is pushed up, these become more and more serious. The use of an enclosed mercury make the break carried by the free end of the strip (Elec. Rev., Chicago, *78*, p. 676; 1921, The Federal Gauge Co., 12 S. Jefferson St., Chicago), promises well, particularly if the strip and break be given a small angular harmonic motion in the plane of the coil to imitate the Gouy arrangement (see below). Such a strip has very little heat capacity and small lag. It probably is subject to elastic hysteresis and other elastic troubles. It has a considerable commercial use, but is little used in scientific work.

Volume Expansion Type. Air or other gas enclosed in a glass or metal container immersed in the bath with a capillary lead out to a barometer has been used. The container volume must be large enough to reduce to negligible amounts the effect of room temperature variation on the capillary and barometer volumes. The range of temperature is great, but the sensitiveness not high or easily increased. A platinum wire in the barometer makes contact with the middle of the meniscus and this is used to control the heater. The barometer may be given an angular vibration, thus introducing the Gouy idea, to lessen the hunting; and replacing the air by a reducing gas lessens contact troubles.

The most used and probably most sensitive of the responding devices is the liquid in glass or metal container. When the movement of the free liquid surface is used to make and break contact, it is important to have maximum surface of contact between bath and bulb. A long metal tube of such a form as not to trap air during the filling serves best. When the Gouy modification is used, a more compact bulb and one made of glass serves almost as well since the larger time lag is here less important and the response is more largely a volume and less a surface effect. The volume employed has been between 50 cc and 1 L. Sensitivity calculations based on size of capillary and bulb give only an upper limit as the other factors such as overshooting (hunting), sticking of mercury to capillary and wire, bulb expansion, all tend to reduce the sensibility.

The choice of liquid is to be determined by (1) temperature range desired, (2) maximum coefficient of thermal expansion, (3) minimum volume—heat capacity, (4) maximum heat conductivity. The following have been used—brine, acetone, benzol, toluol, xylol, kerosene, mineral oil, mercury.

For work about room temperature toluol is very suitable. Its usual habit of blackening the mercury may be practically excluded by boiling in contact with mercury under a return condenser, till further blackening ceases. It is best used without distillation as the latter seems to restore some of the blackening property.

For contact purposes it is necessary to change from the liquid chosen to mercury through some form of U tube as in Fig. 1. The volume of mercury must exceed the greatest total change of volume expected, to prevent liquid escaping or air entering. For electrical use a sealed-in contact must be provided, which may also require insulation from the bath in which the whole apparatus up to the capillary is immersed.

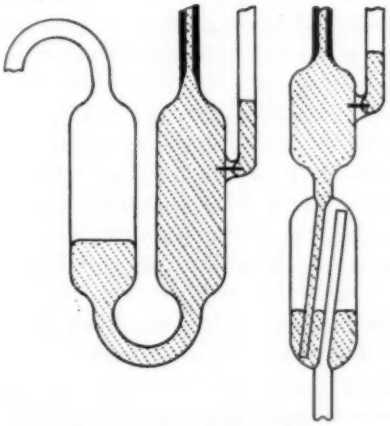

FIG. 1. *Mercury contact device.*

A metal valve for changing the toluol contents for temperature adjustment is readily made. See Fig. 2. The passage past the threaded part of the stem may be provided by a groove filed through its threads and the stem is provided with a removable handle so that the reservoir may be corked. For methods of attaching metal to glass see Am. Chem. Soc. J., *42*, p. 1364; 1920. A satisfactory glass stopcock grease for use in contact with these various liquids over possible temperature ranges is very difficult to find. A glass stopcock for mercury needs very little lubrication and is easier provided, so that the mercury volume may be changed to provide for adjustment, for which the U tube volumes must be correspondingly enlarged.

There are two methods of utilizing the shift of the mercury surface. In the Ostwald type, illuminating gas is led down a tube which projects

down to meet the mercury surface so that the rise and fall of the surface varies the flow, which is led away to a suitable burner provided with a pilot. The minimum diameter of mercury surface is about 2 mm (J. Chem. Soc., London, p. 1030, 1905). The inner tube should be centered and cut off square.

Such an arrangement tends to maintain a true equilibrium state without marked heat waves. In the original form it is mechanically simple. The disadvantages are: lack of sensibility (± 0.1 being fair performance); most gas carries substances which attack the mercury

FIG. 2. *Metal valve.*

so spoiling the flow control—and the gas must be purified; the temperature is seriously affected by the gas pressure which therefore requires regulation; and generally the disadvantages associated with gas flame heating.

The other method of utilizing the shift of the mercury surface is to have it make and break electrical contact with a platinum or iron wire. This may be used to operate an electromagnet which pinches a rubber tube or rotates a stopcock, to reduce the gas flow to the burner. Both maximum and minimum sizes of flame should be separately controllable (e.g. a stopcock in each branch) as the steadiest temperature condition is obtained when the maximum and minimum rates are just far enough apart to cover the actual variation in heat demand.

The diameter of the contact capillary can seldom be profitably made materially less than one millimeter. The time lag of such systems is such that the mercury overshoots and undershoots the contact point often by millimeters and possibly by centimeters. There is thus no

advantage in using a small capillary to increase the sensibility, though it may be used to reduce the necessary volume of bulb. When the mercury is forced up between the wire and the glass in a small capillary, the mercury column is apt to break and the thermostat begin operating at a new temperature.

The principal difficulty in the use of this type—liquid in bulb operating at natural period—is failure at the electrical contact. Such failure leaves the maximum heater operating, the bath temperature climbs forcing mercury or even toluol out of the bulb—so that it sometimes requires hours of labour to restore the previous working state. Contact failure is usually due to fouling of the mercury surface. Reducing the contact spark lessens mercury oxidization. This is accomplished by using the smallest possible potential and inductance in the circuit, by connecting a condenser with the shortest possible leads across the break, by shunting the break with just sufficient non-inductive resistance to let the trip operate. The capillary may be filled with coal gas or hydrogen or reduced air with good results. It may be sufficient to leave a drop of mercury in the conical tip of the capillary which will form a seal around the contact wire and the oxygen enclosed is not sufficient to cause trouble. (J. Am. Chem. Soc., *42*, p. 2058; 1920). Covering the mercury with nonconducting liquid is not effective as such liquids char and also emulsify the mercury. A method of using considerable voltage without sparking is described below.

The bulb liquid may travel for long distances between the mercury and the glass. This may be prevented by a short piece of amalgamated metal tubing sealed inside the glass in the mercury-containing part. Platinum and iron used for this tube are not easy to amalgamate but foul the mercury very little while copper may prove troublesome.

Gouy Modification. (Gouy, J. Physique, *6*, p. 479; 1897; Roebuck, Phys. Rev., (2) *2*, p. 79; 1913; Sligh, J. Am. Chem. Soc., *42*, p. 60; 1920). The constancy attainable by the above devices is limited by presence of heat waves in the bath and its contents and by variation in the average temperature introduced by irregularity in the heat waves. The Gouy modification consists in giving the contact point a vertical reciprocating motion over 1 to 4 mm with a period between 1 and 30 seconds. Each cycle is thus divided into a contact interval of smaller heat input and an open circuit interval of larger input. The ratio of these intervals is determined by the position of the mercury surface. A slow shift of this surface serves to adjust the heat input to meet the varying demand.

If the bath be brought up to the required temperature, the thermostat will first start to operate with its natural period, unless the temperature has been raised sufficiently slowly. With moderate sensitivity and reasonably steady outside conditions, the operation will shift over automatically to the imposed period. If the sensitivity is very high it is generally necessary to damp the natural oscillations by hand manipulation of the heater, till the bath becomes steady enough for the thermostat to assume its function at the imposed period. With high sensitivity sudden outside disturbance may upset the forced operation which also may be regained only by outside help.

Since the mercury surface is not required to make any rapid shifts, the sensitivity becomes dependent on the volume rather than the surface, and large volumes become usable and effective. With the exit of "hunting" smaller capillaries may be used.

It is to be noted that change in energy input is effected by an actual shift in bulb temperature, which was previously the case also. Now, however, it is definite and measurable and can be made small. The magnitude of the excursion to be given the contact point is thus limited and the minimum is set by the irregular sticking of the mercury to the point (White, Phys. Rev., *15*, p. 509; 1920).

The energy input may be made independent of the shift in bulb temperature (Astro. Phys. J., *20*, p. 347; 1904) by using the inequality of on and off intervals to modify the heat input, so as to keep these times equal. It would appear possible also to give up the intermittency of the heating and depend entirely on the inequality of on and off intervals to regulate a continuous energy input. This approaches the ideal in regulation since the temperature change to secure regulation is only temporary and the energy input ceases to be a function of the temperature.

About 0.01°C constancy in the average is rather easily obtained with the simple on and off type. With the Gouy improvement 0.001 is readily obtained where the surroundings are steady, and 0.0001° is quite possible. In the matter of constancy, this Gouy improvement is probably the best obtainable.

The disadvantages are (a) the serious upset in the apparatus due to contact failure in the capillary; (b) the narrow range in temperature set by the properties of the available bulb liquids and of mercury; (c) the large lag.

Relay and Switch. If the energy input is small, the ordinary telegraph relay with platinum contacts may be used. Generally, it is better to use an iron link dipping into mercury in iron cups to short-circuit part of

the series resistance. Currents up to 10 amperes on the 110 v. circuit are readily handled. The mercury is slowly lost by vaporization and also becomes thick and pasty, finally requiring replacing. These troubles may be entirely avoided by breaking the circuit in coal gas and preferably between mercury for both terminals. (Barr, Proc. Phy. Soc., *33*, p. 53, 1920). The arcing is greatly reduced and much larger currents (35 amp.) may be handled.* A simple arrangement is to carry the arm of the relay down through an oil seal to come up inside a coal gas filled space and there operate the link.

Electrical Resistance Thermostat. Either one or two of the resistance coils of a Wheatstone bridge are made of wire having a high temperature-resistance coefficient and are placed in the bath. The remaining resistances are made of low coefficient wire (manganin) and usually will remain sufficiently constant at room temperature. A galvanometer is used to connect the unbalancing of the bridge with a change in the energy input and is the critical feature of the set up. The usual method is to replace the galvanometer mirror by an arm and to pinch the arm at regular intervals between jaws (Randall, Phys. Rev., *28*, p. 142; 1909; Cambridge, Recording Thermometers; and also Leeds and Northrup). The arm reduces the galvanometer sensibility greatly which may be offset by the use of high resistance (1000 ohms) coils and high bridge potential (110 volts): still the sensibility remains well below that of the liquid-in-bulb thermostat. The most promising method for raising the sensibility appears to be to use a light arm to operate a thermopile or a selenium cell (Kolowrat, Journ. de Physique, *8*, p. 495; 1909).

The arm must be caught between jaws, both of which move, and they must be adjusted carefully to release the arm with the minimum disturbance of the galvanometer coil. Two difficulties have to be met—the metals fail to make electrical contact and they stick together. Contact failure takes place with Pt, Ag or W, except for a short time after scraping clean. Sufficient voltage to insure contact produces destructive arcing and sticking. Rubbing the metals together insures contact but is hardly possible mechanically, or the film may be broken down by induction discharges in the neighborhood (J. Wash. Acad. *2*, p. 401; 1921) as with the coherer. But the most effective method is to use the contact to charge the grid negatively in a three electrode vacuum tube while the heater relay is in the plate circuit. 40-50 volts (small dry cells are very suitable) always break down the film resistance and the trifling

* The Federal Gauge Co., 12 S. Jefferson St., Chicago, and Absolute Contractor Corporation, Beloit, Wis., manufacture such switches.

charging current to the grid is without effect on the sticking. Fig. 3 shows a suitable wiring of the entire set up. If the vacuum is good, it is necessary to connect a megohm grid-leak as shown.

Sticking at the contacts may be overcome by arranging the gripping jaws as in Fig. 3. The edges b and c move together and the final contact (between b and c) is made at b by bending the vertically flexible pointer p. The bending force is easily made sufficient to insure separation and this without shaking the coil or straining the galvanometer suspension.

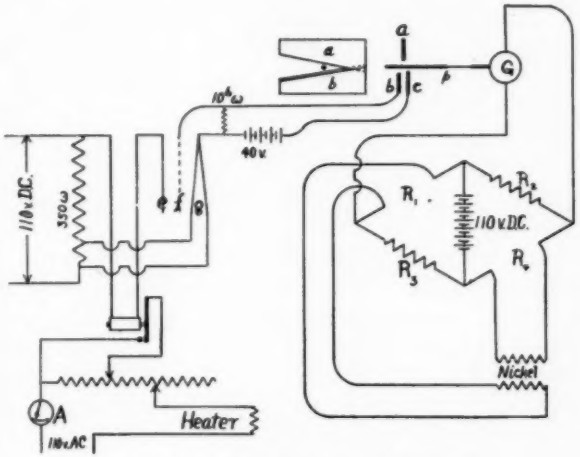

FIG. 3. *Wiring diagram; resistance thermostat.*

In the on and off type the galvanometer pointer is left free only a sufficient fraction of the cycle to allow it to shift position. When gripped in one half the jaws contact is made and the larger current put on (or off). The other half of the jaws are made of insulator so that the weaker current remains on (or off). The relay can be built to make heater contact for either contact or broken contact in the galvanometer and the direction of the galvanometer current must be chosen suitably. The needle thus swings back and forth and the temperature oscillates over a range depending on the adjustment of the average current to that required, the ratio of maximum and minimum currents, and the lags of heater, stirrer and bridge. The best regulation is obtained by minimizing the variability in demand, by setting maximum and minimum inputs as near together as will meet the unavoidable variations and as near to the average demand as possible.

Sensibility is gained by using coils of 1000 ohms or more and a high bridge potential (120 volts) without undue energy input from this circuit. The best available wire is probably pure nickel (Driver Harris Wire Co., N. J.) on account of its high coefficient, mechanical strength and resistance to corrosion. It is best supported on thin mica over a thin walled metal cylinder and may be bedded in Bakelite lacquer for temperatures up to 300°C. For maximum sensibility, both diagonally opposite coils should be in the bath. Very careful insulation of both coils and leads is very necessary especially during any damp season.

The Gouy modification may be applied to this Wheatstone bridge set up, for example, by using continuous jaws each set wider apart on one side as in Fig. 3. As the pointer swings across, it varies the fraction of the period for which the jaws make contact and the maximum heater is on. It is evident that as before the different values of energy input are associated with different temperatures. This may be minimized (1) by sufficient sensibility, or (2) by a small amount of manual attention to keep the pointer near the middle of the swing, or (3) by utilizing the inequality of the on and off portions of the period to adjust resistance in the heater circuit so as to bring these portions back to equality. Evidently also this temperature shift may be made smaller by increasing the ratio of the heating currents, of course with the consequent increase in local inequalities.

Thermocouples. Thermals with a potentiometer may be used instead of a Wheatstone bridge with remainder of the control apparatus as before, and sensibility may be gained by multiplying the number of couples. The necessary control of the temperature of the second junction and the requirement of a steady potentiometer current make the resistance arrangement simpler and generally preferable.

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AUTOMATIC CONTROL OF LOW TEMPERATURES*[1]

By T. S. Sligh

The control of low temperatures differs only in detail from the general principles applicable for ordinary temperatures.

In general the special problems consist of:

(a) The selection of bath and thermo-regulator liquids having physical properties, such as fluidity, boiling and freezing points, etc., suited to the working temperature.

(b) Insulation of the bath from the undesirable access of heat which is especially important because the production of cold is generally a somewhat difficult and expensive process.

(c) Insulation of the bath and its cold accessories against the access and condensation of atmospheric moisture.

For temperatures as low as $-50°C$ a stirred liquid bath, e.g., alcohol, toluene, or gasoline, may be used. Since the use of such liquids is attended with some fire hazard, even at low temperatures, precautions should be taken to prevent explosions and fire. The liquid should be kept closely covered to preclude the posibility of the formation of an explosive mixture and all possible sources of ignition near the bath should be avoided. A mixture of 70 per cent carbon tetrachloride (CCl_4) and 30 per cent gasoline has a flash point at about 50°C and may be used conveniently in the temperature range $-50°C$ to 50°C.[2]

Cooling may be effected by the expansion of ammonia, carbon dioxide, or other suitable substance through an expansion valve and a cooling coil.[3] The regulation may be effected by setting the flow of refrigerant for slight excess cooling and causing a thermo-regulator to automatically compensate for the excess by electric heating. This indirect method is advantageous on account of the great facility with which electric heating can be controlled.

Vigorous and adequate mixing and stirring of the bath liquid are especially desirable in order that the abrupt temperature gradients set

* Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of Physical measurements. See Editorial in this Journal *9*, p. 410; 1924.

[2] B. S. Sci. Papers *18*, p. 707, 1923 (Sci. Paper No. 467).

[3] Osborn, B. S. Bulletin *14*, p. 145, 1917 (Sci. Paper No. 310).

up in the region of cooling and heating may be smoothed out and equalized. The liquid should be drawn from the top of the bath where it has been most exposed to the effects of disturbing influences, past the heating and cooling coils, past the propeller where it is thoroughly mixed, and discharged past the regulator bulb into the bottom of the bath. In this way maximum rapidity of response to temperature changes is secured which is essential to precise control and the tempered liquid is brought into the working space in the bath with minimum exposure to outside influences. As a general guide it will be found that good regulation may be obtained with stirring set up by a propeller in a tube, operating at a speed which will pass all of the bath liquid through the tube three or four times per minute.

A liquid-filled thermoregulator of the helical copper bulb type with setting reservoirs[4] will be found very convenient and effective for temperature control. A volume of about 50 cc of toluene or a similar liquid acting through a U-tube having an internal diameter of 1.5 to 2.0 mm will be found to give all the sensitivity which can be utilized unless the overall thermal lag of the system is reduced below 10 seconds.

For lower temperatures to about $-180°C$ compressed air may be used as the refrigerant. Commercial pentane is sufficiently fluid at this temperature to serve as a bath liquid. A complete system of baths covering the low temperature rage is described in the publications of the Leiden Cryogenic Laboratory.[5]

A carbon dioxide slush bath consisting of a mixture of solid carbon dioxide with a suitable liquid, such as gasoline, alcohol, or ether, affords a fairly constant temperature of about $-78.5°C$ at atmospheric pressure.

Liquid air may be used to produce low temperatures by using the liquid or the superheated or saturated vapor as a bath, or by using the vapor or liquid to provide cooling for a thermostated bath. Owing to the progressive concentration of oxygen in liquid air residues extreme care should be taken to prevent the mixture of this substance with inflammable substances. The Dewar flasks used as liquid air containers may break without apparent cause. This possibility should be recognized and provision made that such an occurrence does not result in disaster. It is advisable where possible to fit containers of thin metal,

[4] Specific Heat of Superheated Ammonia Vapor. Refrigerating Engineering, *10*, p. 149; 1923.

[5] Apparatus and methods in the Leiden Cryogenic Laboratory, Trans. Faraday Soc. 5, *18*, part 2, p. 175, 1922, and Leiden Communications Supplement No. 45.

jacketed by cloth to protect the glass from scratches, into the Dewar flasks. Such liners will prolong the life of the flask by protecting it from sudden changes of temperature, for instance while being filled with liquid air, and constitute a safeguard in case of breakage of the flask. It is extremely hazardous to mix "liquid air," which may be very largely oxygen, directly with inflammable liquids. Electric motors should be so located as not to constitute a possible source of ignition of inflammable vapors and all electric circuits should be guarded by reliable cutout devices.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

Grundzüge der Brillenlehre für Augenärzte.—By A. Brückner O. Ö. Professor der Augenheilkunde an der Universität Basel. VIII+159 pages, price $1.80; Verlag von Julius Springer, Berlin, 1924.

The author draws his inspiration from his study of Gullstrand and the lectures of Moritz von Rohr. He is impressed with the oculist's need of the fundamental principles of optics which have their application in the prescribing of spectacles. Only a mathematician can read Gullstrand so several of his followers have tried to make accessible the results of his work both orally by teaching and by writing. The present book is intended to serve as an introduction for those who are not well trained in mathematics but are willing to follow the derivation of simple formulae.

The three main divisions of the book concern: (1) Elemental optical principles. (2) Spectacle lenses, the human eye as an optical system and their mutual relations. (3) Numerical examples.

Such routine topics as focal length, principal points, size and position of image are taken up in detail and the method of attack is strictly the derivation of practical formulae for calculation. Assuming the Gullstrand dimensions for a normal eye, the derived formulae are applied to the human eye as an optical system. Then the problem includes the provision of a spectacle lens before the eye which needs correction. Attention is given to changes in position and size of the retinal image, principal points, vertex refraction, distance of spectacle lens from the cornea. The exceptional case of cataract lenses is included. This is followed by the principles of accommodation and the influences of lenses upon accommodation, also a section devoted to magnification and the relation between magnification and visual acuity. The astigmatism of the eye is explained and the method of correction is lightly touched. All the important formulae are used in practical examples and the author urges the reader to follow out the numerical equations.

The book is logically planned and keeps closely the limitations laid down in the beginning, namely, paraxial rays, stationary eye, single

vision. Emphasis is justly placed on the ability to carry through numerical problems as a test of the reader's understanding. The most formidable part of the book is the notation, as is usually the case.

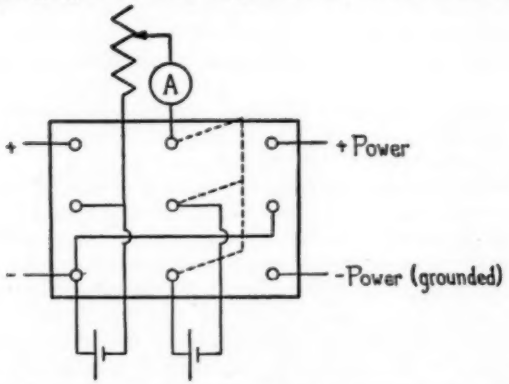
The opportunity was missed to dwell upon the subject of vertex refraction and effective power. This topic is too briefly treated. The student is led to overweigh the importance of the principal points of a lens to the exclusion of the vertex of the rear surface of the lens which is used in practice, and must be used if lenses of different shape are prescribed interchangeably.

It is to the author's credit that in an elementary book the thickness of a lens is not neglected.

In view of its importance, at least a footnote mentioning the other type of astigmatism would be welcome. The astigmatism of a spectacle lens which is due to the obliquity of a beam is not strictly within the compass of a book which limits itself to the stationary eye, but it is well to call attention to it.

A. E. GLANCY

Convenient Storage Battery Circuit.—Kegerreis has described connections for charging and discharging storage batteries, (J.O.S.A. & R.S.I., *10*, p. 474, 1925) using only one double-pole double-throw switch to control all operations. In his arrangement no provision is made for changing from series to parallel connections or vice versa.



In many lines of work, however, it is necessary to obtain large currents by discharging batteries in parallel, while the voltage available for charging is so high that it is more convenient and economical to charge them in series. The accompanying diagram shows how this may be done with two groups of batteries, using only one ammeter capable of measuring current in either direction, one rheostat, and a three-pole, double-throw switch.

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A SET OF CALIBRATION STANDARDS FOR THE PRIMARY EXPERIMENTS OF BALLISTICS

By L. Thompson and N. Riffolt

1. The ballistic laboratory has been subject to a severe handicap in the lack of an established quantitative basis for its fundamental experiments. It is apparent, after a brief survey of the very extreme conditions under which observations are made, that certain imperfections in the tools are unavoidable. The known weakness of the apparatus adds, however, a considerable responsibility for the critical estimation of limitations of the methods. The frequently occurring omission of such criticism is therefore particularly inconsistent.

The nature of some of the more important ballistic experiments is suggested in the following paragraphs in order that the application of the subsequently proposed standards may appear more evident.

Pressures in a gun are still measured by the compression of a copper or lead cylinder, for the reason that no other gauge has been well adapted for routine observation. Notwithstanding the uncertainties of this procedure, no adequate means of calibration has been available for the crusher cylinder. Although the data are sometimes recorded in hundredths of a ton, it is not likely that relative values are significant in tenth-tons and it is doubtful whether, at present, the absolute values have any reliable significance at all, except as a rough record of a past experience prescribing certain limits for safety.

The most commonly noted equipment for the estimation of projectile velocities is that of the Le Boulengé chronograph. The essential parts are a long, falling rod carrying a soft metal cylinder, and an impinging knife actuated by a second, shorter rod. The rods are released successively from two holding magnets at the approximate instant when the projectile penetrates the wire screens causing the circuits to break. The record is a neatly cut gouge in the cylinder. It is customary to record velocities so measured in the exact number of units (foot-seconds), sometimes in tenths. In a recent ballistic paper by several English physicists reference is made to a "nominal accuracy" of one foot-second, but even this is misleading for it suggests, in a way, the possibility of an accuracy of this order. Occasional errors as large as 25 or 50 foot-seconds can and do occur. The probable error could hardly be less than 5 to 10 foot-seconds. Until recently, no statistically significant determination of the precision of this and other chronographs had been

made, although there has been considerable disagreement among the exponents of the various types as to their relative merits.

During the motion of a major caliber projectile through air, the retarding force of the air may be of the order of a ton, or, at a velocity of 2500 foot-seconds, the rate of dissipation of energy is that of an engine of 10000 horse power. The difficulties encountered in making accurate observations of an individual flight are, nevertheless, such that single round values have not been obtained with reasonable precision except in the case of very small projectiles. It appears that the only possibility for such a determination lies in the use of a velocity chronograph of extreme precision, since velocity changes over the required short ranges are comparatively small. Satisfactory wind tunnel experiments can not be made for velocities of the order of those of modern ordnance.

If the motion of a projectile is to be significantly described, it is necessary that the character of the movement about its center of gravity be thoroughly identified. Otherwise the determination of air resistance and corresponding attempts to predict the trajectory of the center of gravity are meaningless from the standpoint of a quantitative science. This phase of the subject is often considered outside the scope of practical ballistics. But no system of ballistics can be practical which is not quantitative. A recent review of a book expressing the former point of view failed to make this clear and yet complained that the differential corrections of ballistics lack significance in their application.[1] The review also suggested that greater uniformity in ordnance is a fundamental requirement. It appears that greater uniformity in the behavior of projectiles is fundamentally dependent on quantitative investigation of their behavior, and it is now well known that the more important remedies are those of design, with particular reference to the factors which determine the character of the motion about the center of gravity.

A rigorous and outstanding contribution to the establishment of a satisfactory analytic basis for the investigation of this problem has been made recently by Professor F. R. Moulton.[2]

An experimental technique has been developed by R. H. Fowler and others, as well as a convenient method for the representation of results.[3]

[1] Shorter Notices. Bull. Am. Math. Soc., p. 469, October 1924.

[2] Not yet published.

[3] R. H. Fowler, E. G. Gallop, C. N. H. Lock and H. W. Richmond F.R.S. "The Aerodynamics of a Spinning Shell." Phil. Trans. Roy. Soc. Series A, *221*, pp. 295-347, 1920.

Measurements are made of the variations in the dimensions of holes punched in a series of cardboard screens placed in the trajectory. While the data so obtained are undoubtedly of great value, such a method can not be considered one of precision, and involves the serious question of the effect of the cards on the motion. Furthermore, if the changes in air resistance and variation in angular deflection of the axis of the projectile are to be correlated with any exactness, the velocity changes must be measured with chronographs of a different order of accuracy. The errors of the Le Boulengé, even when used in duplicate, may be comparable with the total change in velocity.

The apparatus and technique described in the following paragraphs have been developed for the quantitative determination of the essential ballistic data. The instruments have been used in each case for the purpose indicated and the estimates of precision are based on an evaluation of the limits of error inherent in the methods and on data obtained in their use. It is intended to suggest their application as standards, for the comparison of other instruments which may be somewhat better adapted for routine or semi-routine work. Two of the four calibration experiments have been carried out under Proving Ground conditions, and a program for the comparison and dynamic calibration of pressure gauges is being developed, based on the use of the method of section (3).

2. Calibration of Tuning Forks. The fork is an important auxiliary instrument in the ballistic laboratory, being frequently used for the identification of small time intervals, and its careful calibration is required.

The apparatus shown in Fig. 1 has been designed for this purpose and operated with very satisfactory success, establishing the rate in terms of the acceleration of gravity. The registering device is similar to that used with the optical chronograph for the measurement of projectile velocities.[4] A small photographic plate is mounted in a falling projectile (p, Fig. 1a), which is released from the magnet M. The fork is placed in line with the lower part of the trajectory and the optical system arranged as indicated in the Figs. 1a, 3. Light from the slit S is focused on the line of fall of the plate and the record produced as it passes through the optical field is shown in Fig. 2. The slit S is either fixed as in Fig. 3, or formed by shields attached to the fork prongs

[4] L. Thompson, "The Motion of a Falling Chronograph Projectile." Proc. Nat. Acad. Sci., 9, pp. 329-334, 1923.

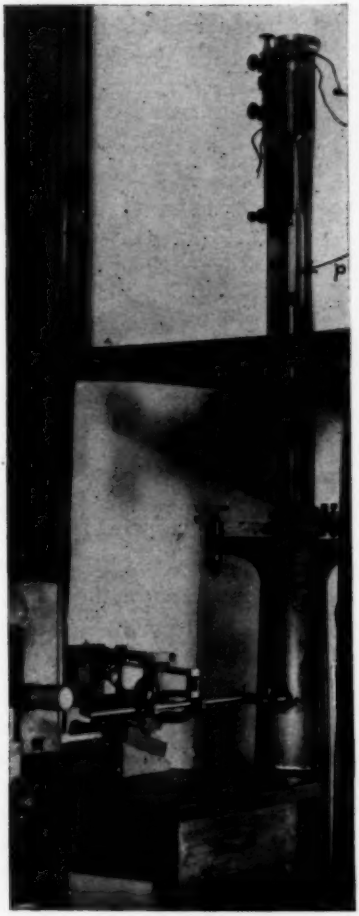

FIG. 1a

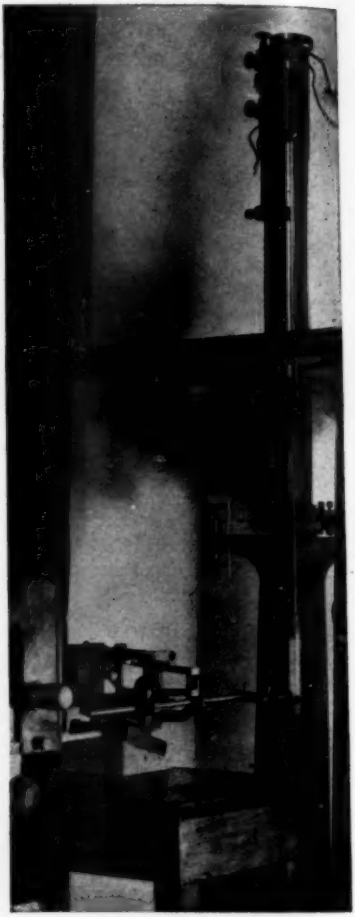

FIG. 1b

Apparatus for the calibration of tuning forks. Fig. 1(a) shows the falling projectile carrying a photographic plate on which the records (figure 2) are obtained. The long rod and plate mounting shown in figure 1(b) are for the determination of height of fall.

after the manner of Curtis and Duncan.[5] The fixed slit is illuminated by the sharp image of another slit source S_1 which moves periodically across the face of the shield containing the slit S. The motion is produced by reflection from a small mirror attached to a torsion filament (which follows the motion of the fork) as described in an earlier paper.[6]

The total height of fall is measured by means of the long rod-mounting shown in Fig. 1b, the photographic plate receiving an accurate record of the position of the image of the slit. The distance from the upper end of the rod to the reference line at the bottom of the plate mounting was determined with a calibrated screw. The effective height of fall is indicated in Fig. 3, and calculated accordingly by means of reference lines on the projectile.

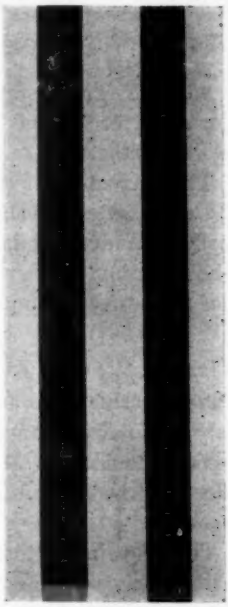

FIG. 2. *Fork calibration records. Time between lines .001 second. Reference line of projectile mounting at lower end of record.*

A report has been made concerning the effect of certain small factors in determining the motion of the falling projectile of the velocity chronograph and the results are also applicable in this case.[4] The holding magnet M, near the instant of release, modifies slightly the motion, the projectile being subjected, in effect, to a varying gravity, the nature of the variation being described by the equation of motion.

$$\frac{dv}{dt} = g - \frac{\mu}{(h+h_0)^2}$$

in which $\mu = gh_0^2$ (since $\frac{dv}{dt} = 0$ at the instant of release). The height of fall to the beginning of the photographic record of the motion is usually of the order of 60 cms. Short time intervals occurring subsequently are given by the expression

$$\Delta t = \Delta t_\infty \left(1 + \frac{h_0}{\sqrt{h_1 h_2}} + \cdots\cdots\right)$$

[5] Harvey L. Curtis and Robert C. Duncan, "A Method for the Accurate Measurement of Short-Time Intervals." B. S. Sci. Papers No. 470, *19*, p. 17, 1923.

[6] L. T. E. Thompson, C. N. Hickman, N. Riffolt, "The Measurement of Small Time Intervals and Some Applications, Principally Ballistic," Proc. Nat. Acad. Sci., *6*, p. 169, 1920.

h_1 and h_2 being the heights of fall for the beginning and end of the part of the record utilized for measurement, and

$$\Delta t_a = \sqrt{\frac{2}{g}}(\sqrt{h_2} - \sqrt{h_1}) \text{ the value for free fall.}$$

A more convenient form is

$$\Delta t = \Delta t_a(1 + K/4g\sqrt{h_1 h_2} + \cdots)$$

in which K is a constant proportional to the unacquired kinetic energy, the result of the modifying effect of the decaying magnetic field of M during the early motion.

The derivation of these expressions has been discussed, giving also the experimental evaluation of the constants K and h_0, as well as the method of determining the slight air retardation of the projectile.[4] The latter involved a wind tunnel experiment for obtaining the constant c of the corresponding expression,

$$\Delta t = \Delta t_a\left(1 + \frac{c}{6}(t_1 + t_2) + \cdots\right)$$

The corrective terms are very small in both cases and need be considered only under circumstances in which calibration errors of .01 per cent or less are significant. If the magnet M is wound for small currents, its effect will be negligible except in a case of extreme precision requirements.

The following factors also affect the value obtained for the frequency of the freely vibrating fork: temperature, amplitude, accidental variation in height of fall, distortion of film while wet, character of slit and imperfect adjustment or focus, and errors of comparator screw.

The apparatus shown in the figures was assembled from the parts of an old Le Boulengé instrument. While the mounting for the fork and optical system was found somewhat faulty, data can be obtained in its ordinary use for which the probable errors are not greater than one part in ten thousand. In order to suggest the inherent capacity of this instrument for determinations of greater refinement, the following data are inserted. These are independent determinations, one set for each plate, using several of the longer groups of lines (1-21, 2-20, etc.) and are fair representations of what may be obtained with such factors as height of fall errors, temperature and amplitude uncertainties, and air resistance eliminated (since these effects are identical for one plate).

See Fig. 2: 500.30, 500.31, 500.33, 500.37 (cycles)
500.33, 500.34, 500.32.

It is intended to note the differences only among the values for each plate. The exactness of agreement of the means for the two plates is accidental since several very small but significant changes in condition occurred, the net effect of which in this case is practically zero. Further improvement may still be obtained by the use of great care in avoiding film distortion, precise calibration of the comparator screw, and an improved slit. The latter is particularly important and the fixed slit method is necessary for the maximum precision. There is a marked improvement in agreement among determinations as the sharpness and general character of the lines are improved.

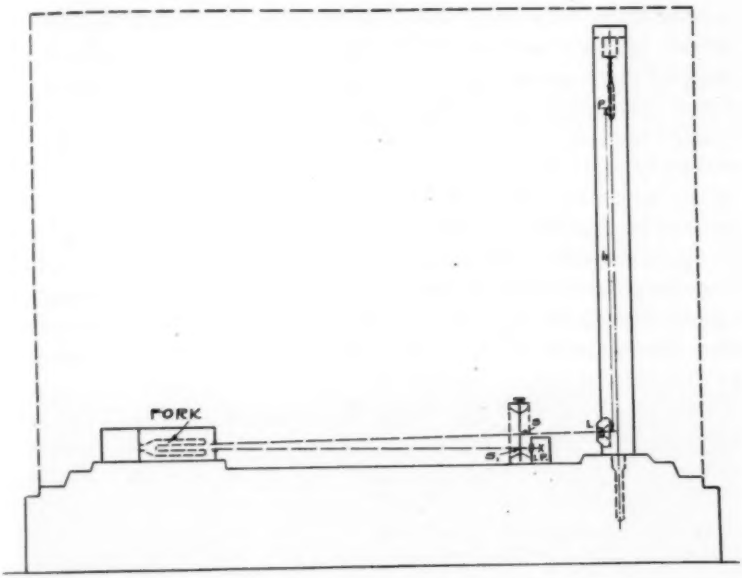

FIG. 3. *Calibration of tuning fork.*

After extensive application of this apparatus it is our opinion that, by means of a specially constructed massive mounting with chamber suitable for evacuation and thermostatic control, the fixed slit form is capable of precision in relative time measurement (the mean value obtained from a series of plates) comparable with that of the most precise pendulum equipment. Examination of the vibration of a fork can be carried out at identical stages in the decay by means of a microscope arranged to observe the width of the illuminated band on the

shield and the control of the release arranged accordingly. The constancy of the elasticity of the fork material under conditions as nearly similar as possible during succeeding experiments, a question which, it is hoped, can be investigated in the near future, appears to be the determining factor relative to the reversibility of the experiment. The possibility of the apparatus being thus used for the relative determination of gravity was suggested by Major William Bowie.

3. The Measurement of Pressure. The determination of pressures in a gun and the corresponding estimation of the indicator card are the weakest points in the technique of the ballistic laboratory. There are, among others, two serious and related sources of error in the use of the crusher gauge. The distortion of the copper or lead cylinder is evidently defined by some function of the time integral of the pressure rather than by its maximum value. An entirely satisfactory calibration can not be accomplished by slow compression. The importance of the kinetic reaction as a component of the total resistance during an extremely rapid displacement of material is suggested by such results as the engraving of hardened steel armor plate by the copper rotating band of a projectile, the sharp punching of a wood slab by a wax projectile (candle) shot from a gun and the smooth hole produced in a glass plate by a high velocity bullet. It is apparent not only that the static calibration of such a gauge is in error but that the magnitude of the error depends on the duration of the interval. The time required for the production of maximum pressure in a military rifle chamber is, in some cases, approximately .0001 second. With larger guns the interval may be many times greater.

The crusher gauge should be calibrated, in order to give relatively significant pressures, by comparison with a pressure-time gauge of established accuracy, for each type of use, that is, for each general class of pressure time curves involved in guns of the various dimensions.

Moreover, there is a considerable need for the development of a pressure gauge which will be capable of registering pressures with a precision comparable with that of velocity measurement and which will be suitable for use in certain kinds of routine work.

There are two types of pressure-time gauges which record electrically, and a third which employs a beam of light.[7] The essential design of a form of the latter instrument is indicated in Fig. 4 and is similar to one

[7] A. G. Webster and L. T. E. Thompson, "A New Instrument for Measuring Pressures in a Gun." Proc. Nat. Acad. Sci., *5*, p. 259, 1919.

developed and used by the writers in obtaining pressure time curves for a .30 caliber military rifle. These are of the order of the shortest total intervals occurring in the range of interior ballistic experiments. The differences in character of the pressure curves are clearly shown in the

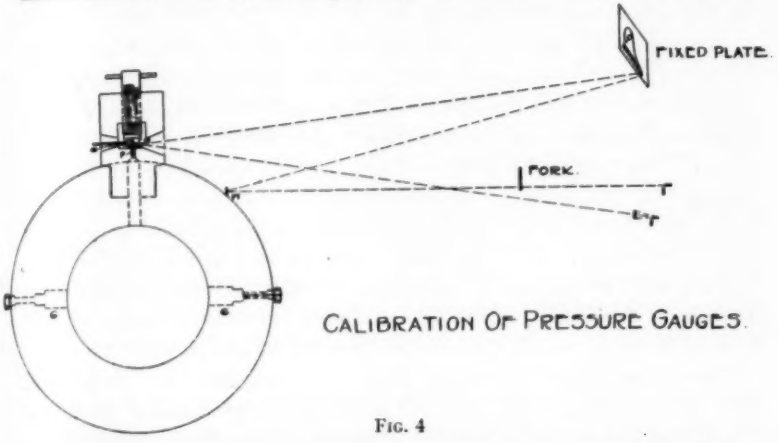

FIG. 4

records. Two of those which we obtained are reproduced in Fig. 5. The important feature of the gauge is that its moving system has a very high natural frequency and considerable damping, the frequency being much greater than that of any component of the force which it is

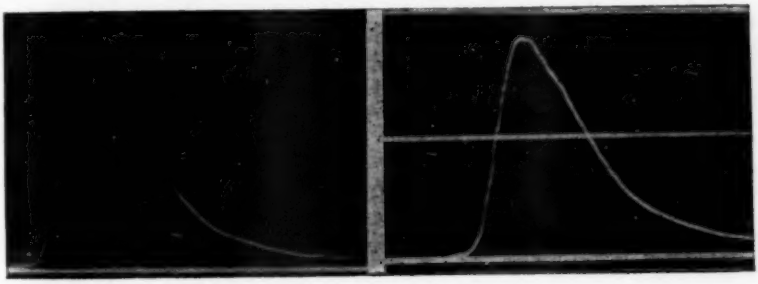

FIG. 5. *Pressure-time curves (reduced), maximum pressure about 20 tons per square inch.*

expected to register. The frequency of the system was designed to be approximately 15000. It may be noted from the records of Fig. 5, which were made with a slightly under-damped gauge and show evidence in several places of a natural vibration of very small amplitude, that the frequency is of this order (since the total time interval for the pressure curve is approximately .001 second).

The electrically recording instruments are the piezo-electric gauge as used by Karcher, Keys and others,[8] and the contact gauge developed by H. L. Curtis and collaborators. The plan for the relative mounting in the gun chamber of the gauges, arranged for a comparison—calibration experiment, is shown in Fig. 4.

The recording system of the optical gauge is arranged to utilize either a fixed or a moving photographic surface, depending on the precision required in identifying time distribution. The relative scale of the parts has been increased in the sketch in order to show more of the detail. The parts consist of a short, light piston (.2″ diameter), an especially tempered spring of rectangular cross section (.6″, .3″, .1″), a slot with blunt knife edges in which the spring is assembled, and a rugged mounting. It is necessary that the slot and spring be constructed with the greatest possible care. The slot must provide an almost perfect fit. The time calibration may be superposed by means of light from the fork slit reflected from the mirror M to the plate.

The calibration of the optical gauge is accomplished by static load, since the condition that this will be adequate is identical with the condition required for the accurate following of rapidly changing forces, namely, that its natural frequency be high compared with those involved in the forces measured. This is not true in the case of at least one type of the electrically recording gauges, and the dynamic calibration is therefore required for that instrument.

It appears that the piezo-electric gauge should be capable of producing an accurate curve for rapidly changing pressures but it is, at present, without an entirely satisfactory method of producing a record. The ballistic galvanometer has been used by Karcher, but this requires differentiation of a very small curve and is not a method of precision, however good the gauge itself may be. The cathode ray oscillograph has been used by Keys, who reports that the curves obtained with this apparatus are true pressure-time curves, contrasted with all others, but evidence establishing this point is not presented. The published records of a few low pressure experiments are rough and fail to demonstrate that the system as a whole is necessarily following the pressure variations with great accuracy.

It is hoped that through such a calibration, at least one form of the electrically recording gauges may be found satisfactory for a class of

[8] J. C. Karcher, "A Piezo-Electric Method for the Instantaneous Measurement of High Pressures." B. S. Sci. Papers No. 445. David A. Keys, "The Cathode-ray Oscillograph and Its Application to the Exact Measurement of Explosion Pressures, Potential Changes in Vacuum Tubes and High Tension Magnetos." J. Frank. Inst., *196*, p. 577, 1923.

semi-routine observation. It is also a purpose of the experiments to calibrate the crusher gauge for such circumstances as can be arranged in the firing.

4. The Measurement of Velocity. Several spark and gravity chronographs have been developed for the determination of projectile velocity. The best of the older types were those of Bashforth and Le Boulengé. The Aberdeen chronograph, one of recent design, employs spark registration, the nearly constant speed drum being occasionally calibrated with a falling ball. The solenoid chronograph is an excellent type for any measurement requiring only less precision than that necessary for air resistance determinations. Its chief limitation occurs in the dependence of the character and interpretation of the record on the manner in which the projectile passes through the screen, a condition which does not, in general, recur exactly at successive screens. Several chronographs are arranged to operate at impact of the air wave accompanying the projectile, an electric circuit being thereby interrupted.

An optical chronograph, consisting of a set of light screens with suitable recording apparatus, has been developed and used for the precise measurement of small differences in velocity.[4,9] In one form, it has measured velocities of nearly a mile per second, in a space of a little more than two feet, with a probable error less than one half foot-second. A new form of this apparatus having a single parallel beam of light, controlled over a path of approximately four hundred feet, has been made the calibration standard for a thorough comparison of the important chronographs now in use. Two entirely independent sets of each type were installed as indicated in Fig. 6. The distance between the two intersections of the beam of light with the trajectory was approximately 160 feet. The records were obtained on a moving film which was calibrated by tuning fork lines. One of these is shown in Fig. 7.

5. Air Resistance. A satisfactory determination of air resistance can be made only with a chronograph capable of measuring velocities with such precision that small differences of ten or fifteen foot seconds will be identified with the accuracy expected in the resistance values. There must be a reliable method of sorting the rounds with reference to the characteristics of flight. The retardation is to be expressed as a function not only of the velocity but of the angular deflection of the axis for a projectile of a specific shape and size. There is no rigorous basis for the use of data obtained for the "law" of resistance with one

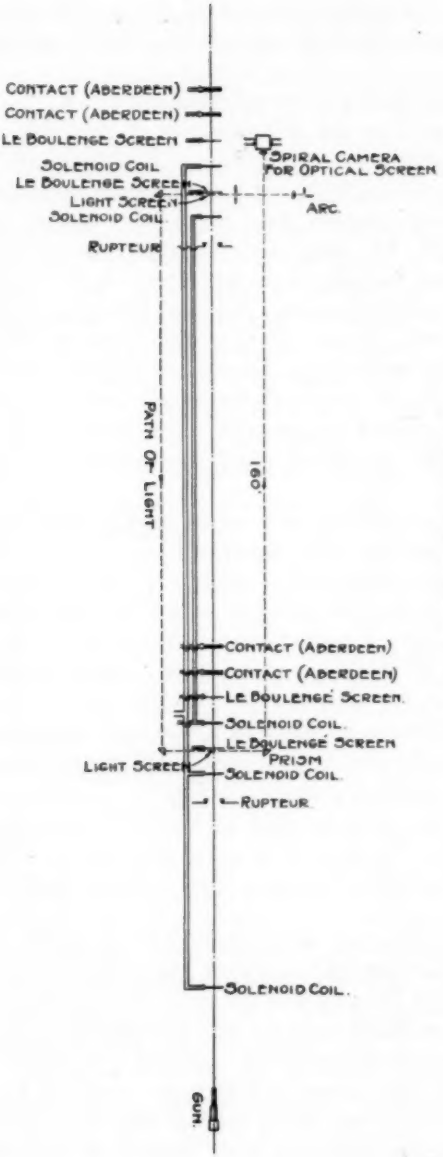

FIG. 6. *Calibration of chronographs.*

FIG. 7. *Optical Velocity Record. Interruptions of beam of light by projectile indicated by arrows.*

type of projectile in expressing the resistance for another of different size or shape. A sufficient variety of quantitative experiments must be performed to constitute a sound structure for interpolation.

An apparatus and technique for such experiments with minor caliber projectiles is indicated in Fig. 8. By increasing the range and modifying the optical system it is likely that it will also serve for larger calibers. An optical chronograph, similar in the essential parts, has been used in the measurement of air resistance with acceptable precision, in the case of small arm projectiles, in a total distance of approximately ten feet.[9] It is desired particularly to emphasize the significance of obtaining these as successive individual determinations rather than averages for many

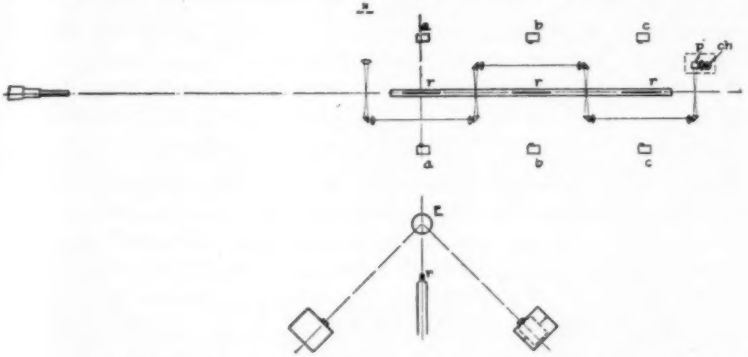

FIG. 8. *Optical apparatus for the determination of air resistance and character of flight of projectiles. E indicates projectile section and r the reference lines. The position of the falling chronograph projectile is shown at ch, the light being controlled in front of it by the double prism and lens at p'.*

rounds. The same order of precision may be obtained for projectiles up to 3 or 4 inches diameter with an observation range of 100 feet. In order for these resistance determinations to have the precision actually indicated by the experimental results,[9] a probable error of 2 per cent or less, it is necessary that the chronograph have measured small relative time intervals of the order of .001 second with an average error not greater than about one two millionth of one second. There appears to be no other chronograph for the measurement of velocity having this qualifying precision.

Four "optical" screens are shown, each consisting of a sharp image of the slit source. Four screens are sufficient to give values of the

[9] L. Thompson. "The Ballistic (Air Resistance) Function." Proc. Nat. Acad. Sci. *10*, p. 279, 1924.

FIG. 7. *Optical Velocity Record. Interruptions of beam of light by projectile indicated by arrows.*

velocity, retardation and rate of change of retardation, at each of these points. Professor Moulton's equations for the convenient computation of these quantities are well arranged for use with the data from equally spaced screens of this type. The only important changes required in the new apparatus (for range of 100 feet) are the substitution of larger prisms, the use of a more powerful arc source and a recording chronograph projectile carrying a longer strip of photographic plate. Massive and shielded mountings are necessary for the support and protection of the lenses, prisms and the parts of the chronograph. No more units are needed for the optical system than were used in the experiment with small arms, although the distances are greater.

The cameras at a, b and c, Fig. 8, are placed for the observation of character of flight and measurement of yaw and precession, and are intended to be slight modifications of the projectile camera developed by Curtis, Wadleigh and Sellman.[10] The principle involved can hardly be improved, as far as the photography of projectiles is concerned. It consists of the simple device of moving a photographic film at the same velocity as that of the image of the projectile, utilizing a rotating focal plane shutter. Practically perfect pictures can be obtained with such a camera having correct mechanical detail. The authors of the paper to which reference is made have underestimated its value in the measurement of axial deflection, apparently because of the results obtained when the camera was not properly adjusted for film speed and direction. We have used the same instrument and occasionally have been fortunate in securing (accidentally, as the mechanism is defective) the approximate film speed desired, in which case the pictures are very sharp, and accurate evaluation of the orientation of the axis can be made. In several series of measurements of major caliber pictures, we have determined axial positions with a probable error considerably less than one degree. In addition to an adequate control of the regulation of film (drum) speed, there is required the placing of three suitable reference lines in the field of the cameras, as shown in the sketch, parallel to the trajectory. These lines will then form a suitable reference to which axial measurements from the several cameras can be referred in order that they may be compared, the relative positions of the projectile identified, and correspondingly, the times. With this arrangement, the cameras may be placed much nearer the trajectory and by use of three sets (Fig. 8) arranged at convenient points near the optical

[10] H. L. Curtis, W. H. Wadleigh and A. H. Sellman, "A Camera for Studying Projectiles in Flight." B. S. Sci. Papers No. 255, *18*, p. 189.

screens, a complete determination of the motion of the projectile about its center of gravity can be made simultaneously with the retardation measurements, without the use of a material screen in the path of the projectile.

PHYSICAL LABORATORY,
NAVAL PROVING GROUND,
DAHLGREN, VA.

The String Galvanometer in Wireless Telegraphy.—Einthoven has succeeded in constructing a string galvanometer with a natural frequency of 300,000. The string in this case is only one millimeter long and is illuminated and observed with the aid of two high power microscope objectives. It appears that attempts have been made to use the string galvanometer for the reception of radio signals but with indifferent success. The signals were received in such a way that the high frequency oscillations were first rectified and the rectified current impulses then passed through the string. Used in this way the string galvanometer has only brought disappointment, the author states, for it reacts to every current of some duration with the same sensitiveness, and even the mildest atmospherics are sufficient to cause trouble. In these experiments the galvanometer was tuned and responded directly to the high frequency wave.

The author shows photographs of the oscillations of a high frequency string whose logarithmic decrement was reduced to 4×10^{-5} by mounting in a vacuum. With such small damping the tuning is extremely sharp and the disturbance due to extraneous influences reduced to a minimum. Such sharp tuning however requires very careful adjustment of the tension on the fiber and close control of the frequency at the sending station. The sensitivity is of the same order as that attained by the use of the telephone. [W. F. Einthoven, Proc. Royal Academy of Amsterdam, *26*, pp. 635-649; 1923].

L. BEHR

Deflections of Alpha-particles in a strong magnetic Field.—This is one of the firstfruits of Kapitza's invention of a method for producing unprecedently strong though transient magnetic fields. The C. T. R. Wilson expansion-method is used to produce the alpha-ray tracks; the familiar apparatus is copied in miniature, the published data being obtained with an expansion-chamber 43 mm in diameter, while another of only 22 mm was built; these are described in detail, likewise the special precautions (in particular, the alpha-particles should be admitted to the chamber at a carefully-chosen moment shortly before the expansion comes to an end) and the graphical method of measuring the curvatures of the tracks. The field strengths used were of the order of 40,000 gauss, sometimes higher, and the tracks

reproduced in the article are very obviously curved. Kapitza estimates the accuracy of his measurements of curvature at from 3 to 7 per cent; the discordances between individual tracks in air are, however, distinctly greater and this he ascribes to the curvatures impressed on the tracks by atom nuclei near which the particles pass; such curvatures are discernible on tracks not influenced by magnetic fields. In hydrogen these deviations are less, as to be expected from the interpretation, and Kapitza plots the curvature of the track as a function of the distance to its terminus, obtaining the material by averaging the data from 12 tracks; these show that the curvature passes through a maximum and then decreases as the particle approaches the end of its range, a strange result only to be explained by assuming that the particles are partially or completely neutralized by adhering electrons over large fractions of their paths near the ends of their ranges. The accuracy of the results is not quite great enough to authorize comparison with other work by other methods, but when improved by using yet higher fields should lead to significant results.—[P. L. Kapitza, Cavendish; Proc. Roy. Soc. *A106*, pp. 602-622; 1924.]

KARL K. DARROW

Bourdon Tube Pressure Gauge.—The theory of the Bourdon tube is investigated in some detail and expressions are obtained for the stresses in the tube and for the direction and magnitude of the displacement of the free end. The latter expressions are in good quantitative agreement with actual measurements, the displacement being found accurately proportional to the pressure. It is pointed out that the linkwork ordinarily used for transmitting the motion of the tube to the pointer causes a deviation from the straight line law which amounts to a maximum of about two per cent. To eliminate this difficulty an arrangement is suggested which consists essentially of a one tooth rack and a one tooth pinion. [C. Sunatani, Technology Reports of the Tohoku Imperial University, p. 19-60; 1924.] L. BEHR

LATENT HEAT DETERMINATIONS*

By Arthur W. Smith

I. HEAT OF FUSION

The determination of the heat of fusion of a substance differs from the usual calorimetric measurements in that no change of temperature is involved in the process of fusion (definite melting point) and therefore it is possible to reduce to a minimum the uncertainties associated with the determination of the thermal capacity of the calorimeter and the measurement of changes in temperature. In all energy measurements it is desirable to express the quantities of heat in ergs or joules, as these are more definite units than "calories." and this is especially convenient when the heat is supplied by an electric current in a heating coil.

Heat of Fusion of Ice. Ordinary ice contains more or less dissolved substance that lowers both the melting point and the heat of fusion. When such ice is warmed up to near its melting point it absorbs more and more heat, due to internal melting wherever the impurities are greatest, and it is difficult to separate the heat of fusion from the heat required to change the temperature of the ice.

Pure ice can be formed by freezing redistilled water until the ice has reached a sufficient thickness and then discarding the remaining water. The ice should be in thin pieces so as to melt readily in the calorimeter. In a warm room the surface of ice is always covered with a layer of water which cannot be completely removed. The pieces of ice should therefore be kept at a temperature several degrees below the melting point, and the mass of the ice determined by weighing it at this temperature.

In the electrical method for determining the heat of fusion the heat required to melt the ice is supplied by an electric current in a coil of wire, and is given by the relation

$$\text{Heat (in joules)} = E\,I\,t.$$

The difference of potential, E, over the coil and the current, I, should each be measured by a potentiometer arrangement and given in terms

* One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of Physical measurements. See Editorial in this Journal *9*, p. 410; 1924.

of a standard Weston cell. The resistance of the heating coil is likely to vary, and therefore it should not enter as a factor in the measurement of the energy. The potentiometer measurements should be taken once a minute or oftener as long as the current is flowing. The number of mean solar seconds, t, that the current is flowing can be measured by a standard clock. As a unit of heat the joule is more definite than the calorie since the international electrical units are very definitely fixed. Should the results of any measurements be desired in calories it can be obtained by multiplying the value in joules by the proper factor. If this factor is later found to be in error it does not invalidate the original measurements.

Inasmuch as the melting occurs at 0°C, the calorimeter and as much of the surroundings as possible should be at this temperature to keep the corrections small. In the method used by A. W. Smith[1] the calorimeter was partially filled with refined kerosene at a temperature several degrees below 0°C. Pure ice was broken into pieces about 1 cm^3 which were kept and weighed at a similar temperature. The weighed pieces of ice were placed in the cold kerosene in the calorimeter by pouring them quickly from a glass beaker down a special funnel before any appreciable change in temperature could take place. The calorimeter and its contents were then warmed up to nearly 0°C., keeping the heating current small enough to avoid raising any part of the contents up to the melting point.

When an equilibrium temperature had been maintained for some hours, and all was in readiness for the melting of ice, the current was passed through the heating coil for a sufficient time (by previous calculation) to surely melt all of the ice present. The heat thus introduced into the calorimeter is used (1) in warming the calorimeter and ice up to the melting point, (2) in melting the ice, and (3) in warming the calorimeter and water from the melting point to a slightly higher temperature. This small change in temperature was measured by an accurate thermometer, and the relatively small amounts of heat expended in (1) and (3) are determined as corrections to (2). This gave

Heat of Fusion of Ice = 334.21 joules per gram.

This result is expressed in terms of a Weston (unsaturated) standard cell whose emf was 1.0193 volts when compared with the standard Clark cell (emf = 1.434 at 15°C) at the Bureau of Standards. In terms of the present value of the international volt the emf, of this

[1] Arthur W. Smith, Phys. Rev. *17*, p. 193; 1903.

cell would be 1.01845 international volts, and making this change and reducing the weighing to vacuum gives

Heat of Fusion of Ice = 333.23 international joules per gram mass = 79.63 mean calories per gram mass, if a mean calorie is equivalent to 4.185 international joules.

Another form of calorimeter has been used at the Bureau of Standards[2] in which no liquid is required. The electric heating coil is built into the thick copper wall of the calorimeter, the copper acting as the calorimetric medium for the transmission and distribution of the heat. Temperature changes are measured by an electric resistance thermometer likewise imbedded in the wall. The calorimeter is suspended within a jacket that is surrounded by a well stirred bath of gasoline that can be maintained at any temperature between $-55°C$ and $+40°C$. The heat developed in the heating element is measured directly in electrical units by means of a potentiometer and a standard cell.

The ice specimens were contained in a metal cell which fits inside the calorimeter. Several radial copper vanes are attached to the interior surface of this cell to aid in the distribution of the heat. Starting with the calorimeter and the ice a few degrees below 0°C, sufficient heat is generated to melt the ice and bring the final temperature to a few degrees above 0°C. The mean of three determinations gave

Heat of Fusion of Ice = 333.64 international joules per gram mass = 79.72 mean calories per gram mass

By using a different oil for the bath this calorimeter can be used at higher temperatures. It could then be adapted to measure the heat of fusion of any substance that melted at a temperature at which the surrounding bath could be maintained.

It is far more convenient to work with apparatus at ordinary room temperatures than at very low or very high temperatures, and in a careful determination of the heat of fusion of ice at the Bureau of Standards[3] a calorimeter with water a few degrees above room temperature was used. The handling of the ice required the greatest precaution to be sure that the entire mass has a uniform temperature and does not gain any heat while it is being transferred to the calorimeter. The ice was kept overnight in a chamber at $-0.72°C$ and weighed while still at this temperature by being suspended by a wire from one end of the balance which was in the warm room outside. When the calorimeter is in

[2] Dickinson and Osborne, Bull. Bureau of Standards, *12*, p. 23, 1915-16.
[3] Dickinson, Harper and Osborne, Bull. Bureau of Stand. *10*, p. 235, 1914.

readiness the cover is opened and the hollow cylinder of ice quickly transferred from its cold chamber to the water in the calorimeter. The proper amount of heat is immediately supplied by an electric current in a heating coil so that the final temperature is very nearly the same as the initial temperature. There is an advantage in this higher temperature as the ice will melt quicker than when the calorimeter is kept within a degree or so of the freezing temperature. The heat required to warm the ice from $-0.72°C$ to the melting point and that required to raise the resulting water to the temperature of the calorimeter must be computed as a large correction to the measured amount.

The calorimeter proper was surrounded by a water jacket and cover through both of which water at a constant temperature was continually circulating. No insulating material was used in the air space between the calorimeter and the surrounding jacket, and the loss of heat depended directly upon the difference of temperature between them.

The temperature of the calorimeter was measured by a resistance thermometer, and the difference in temperature between the calorimeter and the jacket was determined by means of a thermoelement. The heat corresponding to the small change in temperature of the calorimeter, the heat loss or gain to the jacket, and the heat lost when the cover is opened a moment to receive the ice, are treated as corrections to the total measured energy that was supplied by the electric current.

The mean of 13 experiments gave

Heat of Fusion of Ice = 79.69 mean calories per gram mass
= 333.49 international joules per gram mass,

if the ratio of the mean calorie to the joule equals 4.185.

METHOD OF MIXTURES

This method is simple in theory and it has been extensively used, especially in the earlier investigations.[4] It is far more convenient to work with apparatus at ordinary room temperatures than at very low or very high temperatures. The warm water of the calorimeter furnishes whatever heat is needed to melt the substance and bring it to the final temperature of the calorimeter. This heat is measured by the change in temperature of the calorimeter which is simple enough for approximate determinations but is not adaptable to measurements of precision. Ice can be placed directly into the water, as can other substances that are not affected by the water. Salts that would be dissolved in the water (with heat of solution) can be enclosed in a closed receptacle.

[4] *e.g.* Person, Ann. de Chemie, *21*, p. 295, 1847; *24*, p. 129; 257, 1848.

If the temperature of fusion is above 100°C. the method of mixtures with water can still be used by having a small inner vessel within which the substance can be placed. By using different initial temperatures for a series of similar experiments both the specific heat and the heat of fusion (solidification) can be computed from the measurements. Large corrections, however, are introduced by the heat required to bring the substance to the comparatively low temperature of the calorimeter in addition to the usual uncertainties of this method. Many of the values now found in tables of constants were determined in this way.

The heat gained or lost by the calorimeter to its surroundings is determined by observing the change of temperature for a period before and again after the experiment proper. As the temperature usually changes rapidly at first and slowly approaches its final temperature, the calorimeter should be arranged so that the final temperature will be the same as that of its surroundings. In this way the large initial correction is multiplied by a short time, and the longer period at the end is multiplied by the smaller rate of heat loss, thus keeping the total heat correction from being too large. In other special cases, such as when the calorimeter quickly reaches its final temperature, other ways of computing the cooling correction may be advantageous.[5]

The calorimeter used for the electrical method at the Bureau of Standards was also used in the method of mixtures.[6] For this purpose the heating coil is omitted, and the change in temperature is several degrees when the ice is melting. Most of the heat required to melt the ice and raise the temperature of the resulting water to the final temperature of the calorimeter comes from the cooling of the water originally in the calorimeter. Therefore the amount of cooling and the heat capacity of the system require exact determination, while all the other terms entering the computation are relatively small and permit of more or less approximation. The cooling correction is very much larger than in the electrical method, being 1 to 2 per cent of the total heat measured.

The mean of 8 determinations by the method of mixtures gave

Heat of Fusion of Ice = 79.61 calories (15°) per gram mass
= 79.59 mean calories per gram mass

which is measured directly in terms of the thermal capacity of water and does not involve the ratio of the joule to the calorie.

[5] See H. C. Dickinson, Bull. Bureau of Standards, *11*, p. 189, 1915.
[6] Bull. Bureau of Standards, *10*, p. 258, 1914.

METHOD OF COOLING

The method of cooling can be used to measure the heat of fusion at high temperatures. In this method two similar crucibles, in similar surroundings, are used, one containing the melted metal for which the heat of fusion (solidification) is desired and the other containing some metal that has no change of state at the temperature that is being used. The number of seconds required for each crucible to fall through a given temperature range is proportional to its supply of heat, which in the case of one of the crucibles includes the heat set free by solidification. The heat lost by the other crucible is the product of its thermal capacity and the change in temperature.

II. HEAT OF EVAPORATION

By the heat of evaporation of a substance is meant the amount of heat per gram mass of the substance (weight in vacuum) that is required to change the substance from liquid, usually at the boiling temperature, into vapor at the same temperature. At any temperature there is some evaporation, and the corresponding heat per gram mass is not the same as at the boiling point.

The heat of evaporation can be determined in either of two ways. The vapor can be condensed to the liquid form within a calorimeter and the heat liberated measured by the rise in temperature, or the inverse procedure can be used by allowing the evaporation to take place in the calorimeter and supplying the necessary heat by an electric current in a heating coil. In many respects the former is the simpler, and the earlier determinations were made by this method of mixtures. This involves the measurement of the rise in temperature of the calorimeter by means of thermometers, and a determination of the thermal capacity of the calorimeter and its contents. The heat lost or gained by radiation and through the conduction and convection of the surrounding air is determined by measuring the change in temperature for several minutes before and after each experiment.

The amount of vapor condensed in the calorimeter is determined by weighing the condenser. In boiling a liquid there is often some of the liquid carried along with the vapor in the form of fine drops or mist, and this should not be counted as evaporated vapor. Various forms of traps to catch the water and allow only the vapor to enter the calorimeter have been used with more or less success.

In Regnault's experiments[7] the effect of some of the sources of error was reduced by condensing large amounts of steam, and his results were the most accurate of the time.

By using a small flask, heated by a gas burner, directly over the condenser and calorimeter, Berthelot[8] showed that accurate results could be obtained with small amounts of vapor. One serious difficulty in all of these experiments is the premature condensation of some of the vapor before it enters the calorimeter. By placing the boiler close to the calorimeter there is less opportunity for this condensation. On the other hand the close proximity of the gas burner and hot boiler increases the amount of heat received by the calorimeter from its surroundings. In several respects the apparatus of Berthelot was too simple. The vapor that came from the boiler before boiling began was allowed to enter the calorimeter, and the steam was undoubtedly superheated in passing down through the tube surrounded by the gas flame.

Kahlenberg[9] improved Berthelot's boiler by heating the liquid with an electric current through a resistance coil that was immersed in the liquid. Thus the calorimeter was disturbed only by the presence of the hot boiler itself, and this was shielded by being surrounded with a thick layer of cotton batting.

One of the most serious causes of error in all calorimetric work is the more or less uncertain correction for the cooling or warming of the calorimeter during the course of an experiment. Therefore Richards and Mathews,[10] while still using the method of mixtures, arranged a water jacket around the calorimeter that could be warmed at the same rate as the calorimeter, and hence the calorimeter was always in a chamber that was at the same temperature (supposedly) as itself. When the temperatures are changing it is difficult to be sure that they are both identical, but as any differences are small the undetected loss or gain of heat by the calorimeter is not large. A curious innovation is the use of the heat of reaction between acid and alkali for warming the surrounding bath. Another improvement was the placing of a hood over the top of the exhaust tube through which the vapor left the boiler. This hood was entirely surrounded by the steam in the boiler and therefore would not cause condensation of the vapor passing through it, and as the stream of vapor had to make a turn of two right

[7] Regnault, Mem. de l'Inst. de France, *21*, p. 638; 1847.

[8] Berthelot, Jour. de Physique, *6*, p. 337; 1877.

[9] Kahlenberg, Jour. Phys. Chem. *5*, p. 215; 1901.

[10] Richards and Mathews, Proc. Am. Acad. Arts and Sci. *46*, p. 519; 1911.

angles the drops of water would be unable to follow the vapor into the calorimeter. Mist of a sufficient degree of fineness could follow the stream of vapor around the bend.

These experiments of Richards and Mathews illustrate a method by which unknown errors can be eliminated from a series of measurements. It was noticed that smaller values for the heat of evaporation were obtained when the rate of evaporation was slower. There thus seemed to be some error that was proportional to the time required to evaporate a gram of water. Plotting all of the results on a chart with the times required to evaporate a gram of water as abscissae, and the corresponding measured values of the heat of evaporation as ordinates, gave a linear relation. Extending this straight line back a short distance to the point of zero time to evaporate one gram gave a corresponding value for the heat of evaporation, and this value is free from the errors due to the time required to evaporate the water.

Other improvements consisted in building the boiler within a double-walled vacuum vessel and the use of electric heating. Premature condensation of some of the vapor is one of the principal sources of uncertainty in these experiments. This double-walled boiler was actually set into the top of the calorimeter, thus reducing to a minimum the distance from the boiler to the calorimeter. The vapor was condensed in a spiral tube of block tin, with a tin reservoir at the bottom to collect the water. By removing the coil and condenser, drying and weighing them, the mass of vapor condensed is determined.

The heat measured by the calorimeter includes the heat given out by the condensed water in cooling to the temperature of the calorimeter, which can be computed if the specific heat of the water over this range of temperature is known. The final result,[11] corrected to zero time for evaporation, and the weight in vacuum, is

Heat of Evaporation of Water at 100°C
= 539.5 calories at 15°C per gram mass
= 539.4 mean calories per gram mass.

One of the limitations of the method of mixtures appears in that the heats of evaporation of several other liquids can not be given until the specific heats of the liquids have been determined.

ELECTRICAL METHODS

It is coming to be recognized more and more that there should be as little change in temperature as possible in precise calorimetric deter-

[11] Mathews, Jour. Phys. Chem. *21*, 569; 1917.

minations. It is desirable to have the calorimeter and all of its contents remain at a constant temperature, and to have the surroundings at this same temperature. The heat lost by radiation and convection is then reduced to a minimum, and the thermal capacity of the apparatus does not enter into the computation.

One of the most satisfactory realizations of this idea is the calorimeter built by Griffiths.[12] This was designed to reduce to a minimum the errors arising from (1) thermometry, (2) variations in the specific heat of water, (3) thermal capacity of the calorimeter, and (4) loss or gain of heat by radiation, conduction, and convection of the air.

The calorimeter was completely surrounded by a nickel plated steel enclosure, forming the bulb of a mercury thermoregulator that maintained a large water bath at a constant temperature to within 0.01° C. The space around the calorimeter was made a fairly good vacuum, which reduced the convection effects of the air. A refined oil was used for the calorimetric medium. Immersed in the oil was a spiral silver tube, 18 feet in length and leading from a silver flask at the center of the calorimeter to an air pump outside. The heat was supplied by an electric current in a resistance coil near the flask and was measured in electrical units. The current through this coil was continually kept at such a value that the electrical difference of potential across the coil was the same as the cmf of an integral number of Clark standard cells in series. Thus while the Clark cells furnished no current they served to measure accurately the heat generated in the resistance coil, and which was computed from the relation, $\text{Heat} = (nE)^2 t/R$ joules. The value of E was taken as 1.4342 volts at 15°C. The time, t, that the current was flowing was automatically registered on a chronograph in connection with a standard clock.

A weighed amount of water in a glass tube was placed in the calorimeter before the experiment began, and in order to control the rate of evaporation this water was allowed to enter the silver flask drop by drop just fast enough to use the heat produced by the electric current. Since both the heating and the cooling processes take place within the calorimeter, only the slight difference between the two remains to be measured. The vapor passed out through the long spiral silver tube and thus attained the temperature of the calorimeter before leaving it. The experiment continued until the last drop of water had just finished evaporation.

[12] E. H. Griffiths, Phil. Trans. A. *186*, p. 261; 1895.

The principal correction was for the heat supplied by the stirrer, which was determined and added to that from the current. The other corrections due to heat lost by radiation, etc., and to the slight change in temperature of the calorimeter, amounted to less than 1/1000th of the heat supplied by the current, and an error in determining the amount of this correction has a very small effect on the result.

Henning[13] also used an electric heating coil to boil the water within a calorimeter. The boiling water served as the calorimetric medium and the steam was collected at the top of the calorimeter and carried down through the boiling liquid to a 3-way valve by which it could be directed into either of two condensers. After the boiling had been going on uniformly for some time the valve was quickly turned and the steam condensed in a weighed condenser for a measured interval of time, at the end of which the steam was diverted back to the other condenser without interrupting the evaporation or the boiling.

The value[14] found by Henning is

Heat of Evaporation of Water at 100°C
= 539.1 calories (15°) per gram mass
= 2256 international joules per gram mass.

By reducing the pressure within the calorimeter the water could be made to boil at a lower temperature, and the heat of evaporation at this temperature determined.

There is a continual plaint running through all of these accounts regarding the presence of water in the vapor that is being condensed. This water may come from the boiling water along with the steam, or it may be from steam that has been condensed by passing through colder parts of the apparatus. It may even be a mist throughout the vapor due to a slight chilling and so fine that it is carried along with the vapor in spite of traps, etc. No one seems to be sure that the precautions taken to avoid moisture in the steam were fully successful.

Water in the steam affects the results in two ways. When the steam is condensed in the calorimeter any water present is collected and weighed along with the condensed steam, but without giving its heat of evaporation (condensation) to the calorimeter. Therefore the mass of water is too great and the computed value of the heat of evaporation is correspondingly too low.

When the water is evaporated in the calorimeter it does not matter in what form it gets into the condenser provided it all reaches the

[13] Henning, Ann. d. Phys. *21*, p. 849; 1906.
[14] Henning, Ann. d. Phys. *58*, p. 759; 1919.

condenser and is weighed. But in vigorous boiling there is some spray thrown into the steam and some of this may be carried out of the calorimeter without evaporation. Here again the amount of water weighed will be too large and the computed value of the heat of evaporation will be too low.

In the experiments of A. W. Smith[15] hot water (98°C) was allowed to evaporate into a stream of dry air that was warmed to the temperature of the water and passed through the calorimeter. A surprisingly small amount of air is required when the water is thus near to the boiling point and there was no difficulty in evaporating 40 grams per hour from the smooth unruffled surface of the water.

The mixture of air and steam was collected by a tube at the top of the calorimeter and carried through a coil in the water below to make sure that it had the same temperature as the water. After passing through the surrounding steam jacket a 2-way valve could direct it into either of two weighed condensers and H_2SO_4 tubes. In order that there should be no condensation of vapor in this valve or the connecting tubes they were enclosed in a box where the temperature was maintained at 130°C. Any heat added to the vapor after it leaves the calorimeter does not matter, but it is essential that no vapor is condensed on the way and so fails to reach the weighed condensers.

After collecting the vapor for an hour the stream is diverted to the other set of weighed condensers and tubes for the next hour. In the meanwhile a fresh condenser and tubes are substituted for those that have been used. Thus there are several determinations of one hour each following each other with no intermission. Such a series of successive determinations is more valuable than the same number of experiments with an interval between them, because whatever thermal uncertainties may be left at the end of one run are carried forward to the next, and are corrected with certainty in the average.

The heat lost or gained by the calorimeter through all of the various ways of radiation, convection, etc., was corrected for by combining the results of two similar experiments that were performed with the barometer and temperatures as nearly alike as possible. If the various sources of heat could be computed the computations would be the same for both, the only variation being that a smaller amount of water is evaporated in one of them. If in the first experiment W' grams of water were evaporated by $H'+h$ joules, where H' is measured and h is

[15] Arthur W. Smith, Phys. Rev., *33*, p. 173; 1911.

the heat from outside, and in the second W'' grams are evaporated by $H''+h$ joules, then we can say that $W'-W''$ grams have been evaporated by $(H'+h)-(H''+h)=H'-H''$ joules. In this way h is eliminated.

The result of 40 experiments taken in pairs in this way and corrected to 100°C gave

Heat of Evaporation of Water at 100°C
= 2261.5 international joules per gram mass
= 540.4 mean calories per gram mass.

This value is larger than is usually given for the heat of evaporation at 100°C. In order to see whether this is due to some peculiarity of the method or the apparatus, another 8 experiments were made. The only difference was that the stream of air was reduced while the heating was the same. This means that the same amount of water (36 grams per hour) is evaporated as before but now the water boils in the usual manner. The steam passes through the same tubes and is collected in the same condensers. Allowing for the necessary corrections by taking the differences, pair by pair, as before, the results from these experiments when the water was boiled gave

Heat of Evaporation of Boiling Water at 100°C
= 536.4 mean calories per gram mass.

This seems to indicate that there is a real difference between the two ways of evaporation, and suggests that the quiet evaporation from a smooth surface of the liquid may give the truer value.

While the case of water has been mainly used, the electrical methods can be used equally well for the determination of the heat of evaporation of other liquids.

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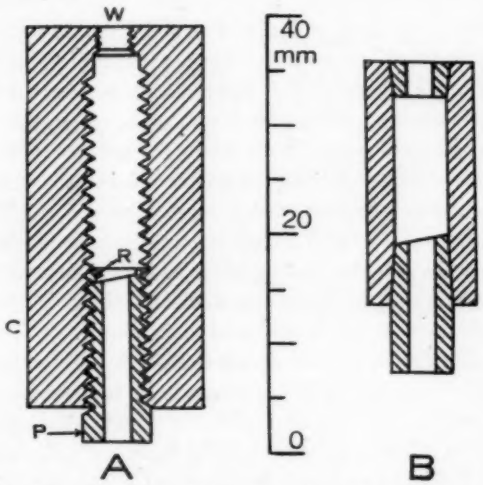
A BLACK BODY FOR OPTICAL PYROMETER CALIBRATION

By Howard S. Roberts

When one of the standard metals is being used to calibrate an optical pyrometer it has been customary to proceed according to one of two methods: 1, to take readings with the pyrometer sighted on the bottom of a black body immersed in the melting or freezing metal; or 2, with the pyrometer sighted into a black body whose temperature is known from the indication of a thermocouple freshly calibrated in situ by the wire method. The first method is open to the objection that a large amount of the standard metal must be used and kept free from contamination; and the second method, to the objection that the temperature of the black body is known only indirectly and may be subject to considerable uncertainty because of changes in the calibration of the thermocouple. The method to be described meets both of these objections and if carefully carried out may be expected to give nearly the accuracy of method 1.



A—Black body of Graphite for use with metals that do not form carbides. B—Black body of porcelain for use with metals that do form carbides.

A suitable black body for this new method is shown at A in the figure. *C* is a hollow cylinder of graphite having a screw thread on the inside to provide the effect of a series of diaphragms. The upper end is constricted

to form an opening W, 2.5 mm in diameter. A hollow plug, P, also of graphite, screws into the lower end of the cylinder and has a shallow recess R with an oblique bottom cut in its inner end. A disc cut from a sheet of the standard metal is placed in this recess, the black body put into a furnace with its axis vertical and the pyrometer sighted down through the opening W.

Until melting begins no details of the disc are visible and, on account of the obliquity of the disc, specular reflection from its surface consists of light from the wall of the black body. However, as soon as any of the material has melted, dark lines and patches appear, caused by reflection of the dark window in the polished surface of the molten portions. With a little practise and a docile furnace it is usually possible to match the pyrometer filament to the disc at least four times before the disc finally tumbles down the hole in the plug, thus giving a positive indication that it has melted.

This graphite black body is only suitable for use with metals that do not form carbides, such as silver, gold, palladium, platinum, etc. For other metals such as nickel and iron, or where the furnace might be injured by the presence of considerable quantities of carbon monoxide, the black body is preferably made of porcelain or of an oxide such as thoria. A construction that has been used successfully up to the palladium point is shown at B. Here a tube of Marquardt porcelain has a smaller tube ground into each end. The inner end of the lower tube is cut off obliquely and forms a seat for the disc. In order to improve on the low emissive power of the porcelain the interior is coated with a salt, such as a nitrate, which gives a colored oxide on heating. The process is repeated until a dark coating is secured. It is desirable where possible to make the coating of an oxide of the metal to be melted, but for the noble metals chromium oxide obtained by painting with ammonium dichromate has been found satisfactory.

From the standpoints of obtaining the black body condition and of ease of construction the graphite form is to be preferred. Graphite has a very high emissive power and a high thermal conductivity so that there can be very little variation in brightness over the inner surfaces. Acheson graphite rods may be machined with ordinary tools and the threads cut with taps and dies. Porcelain, on the other hand, has a low thermal conductivity and particular attention must be paid to the equalization of temperature over the black body.

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CARNEGIE INSTITUTION OF WASHINGTON,
NOVEMBER, 1924.

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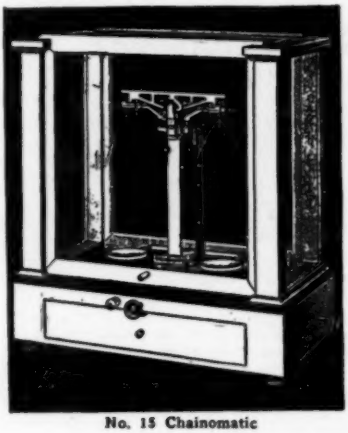

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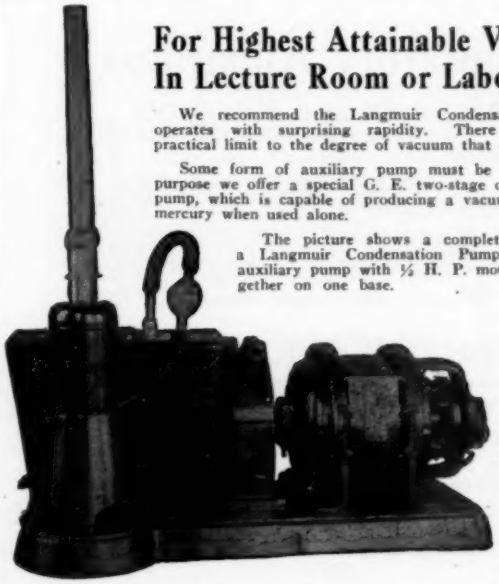

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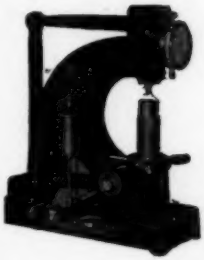

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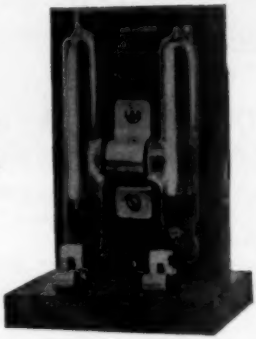

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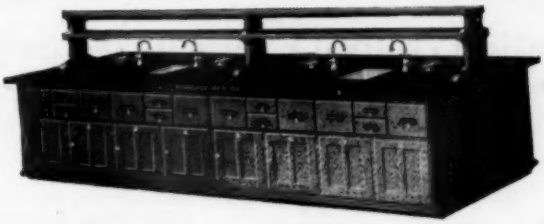

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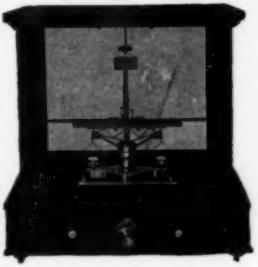

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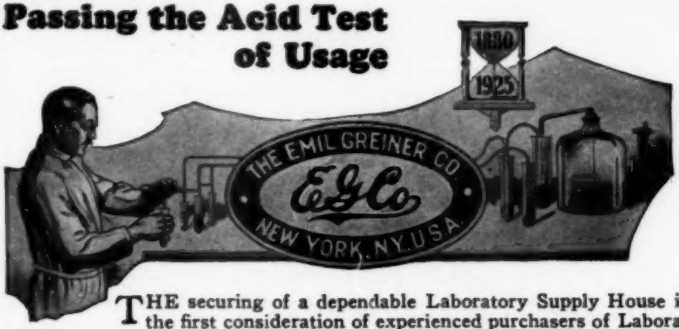

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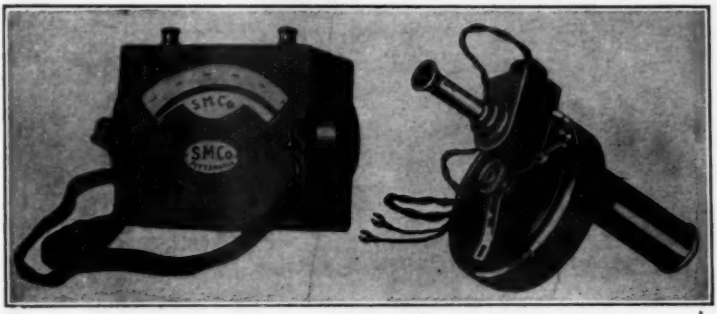

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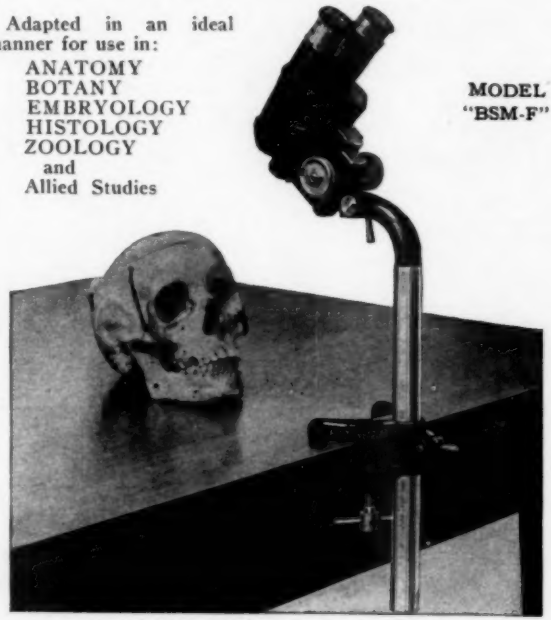

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